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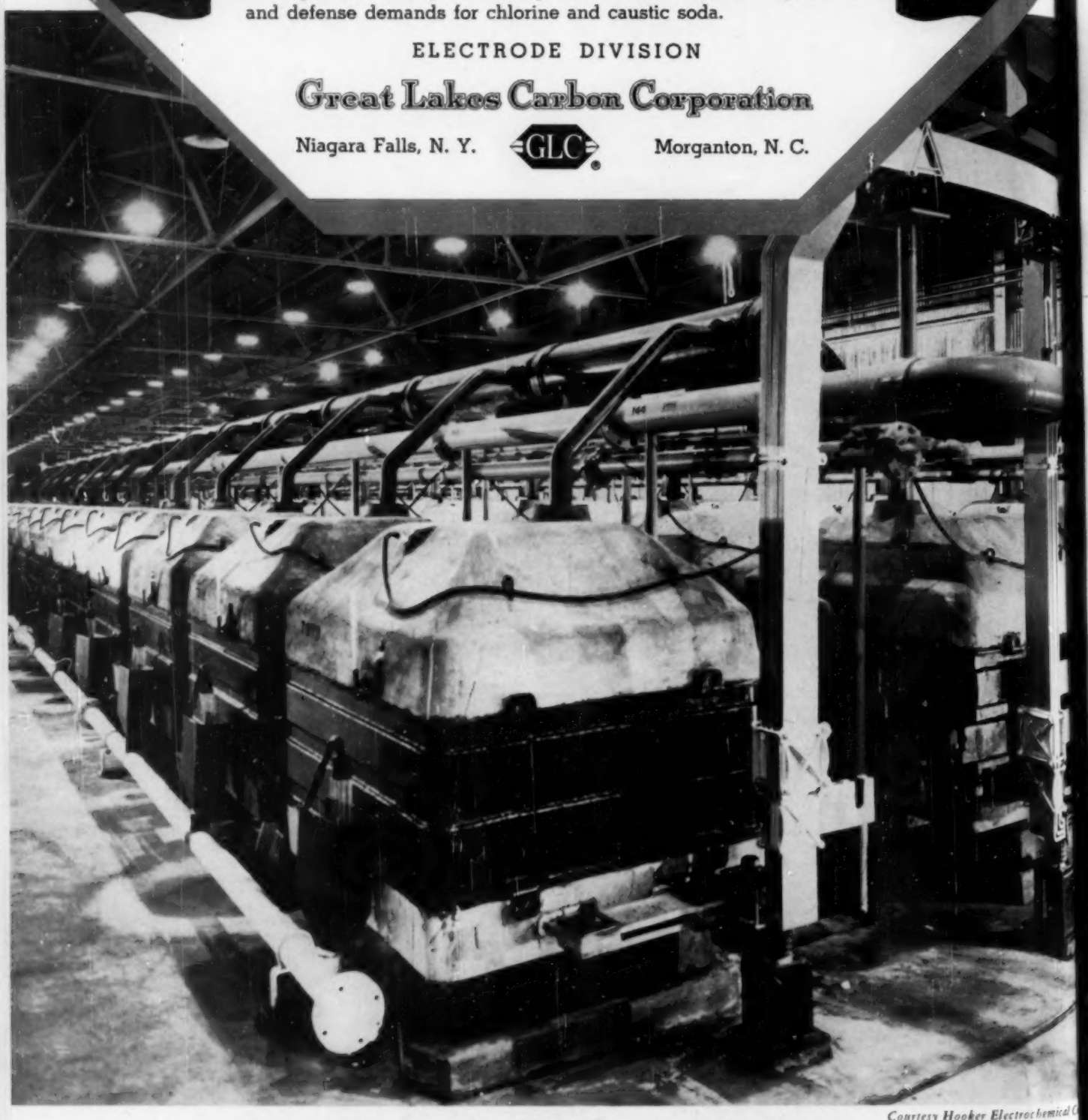

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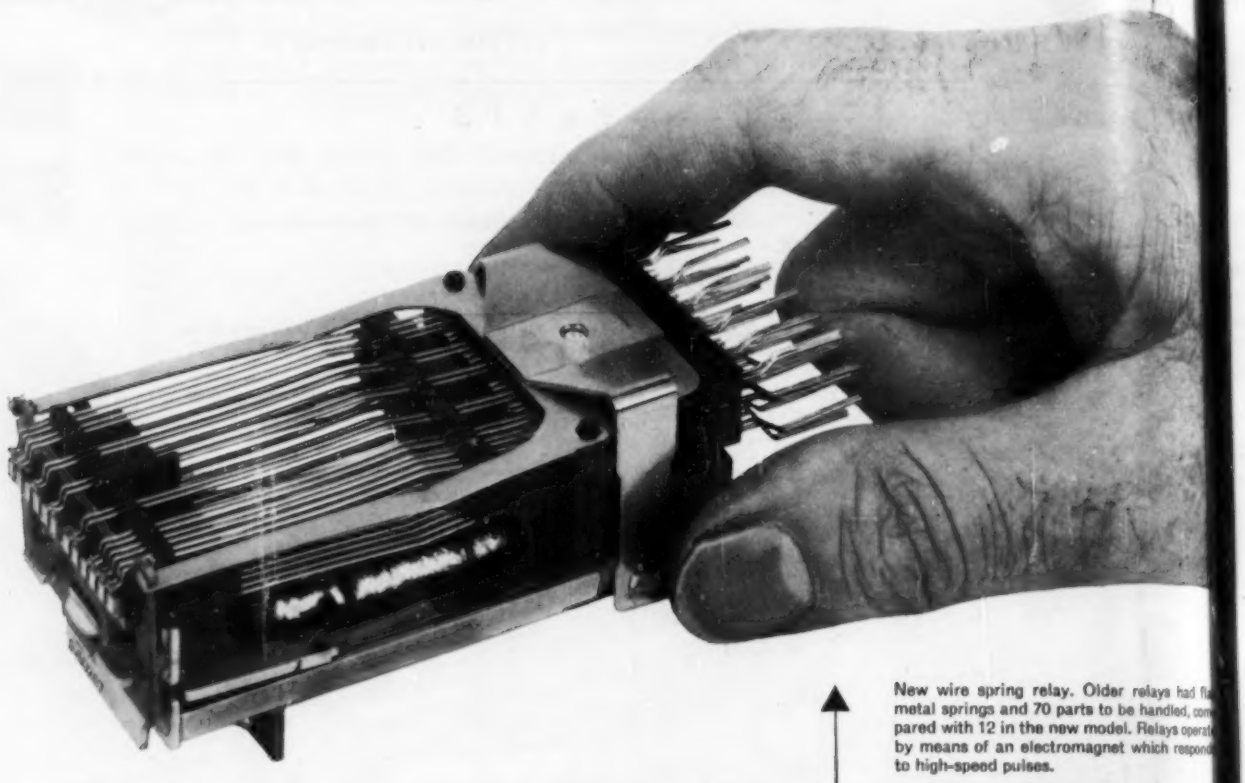
It splits seconds even faster

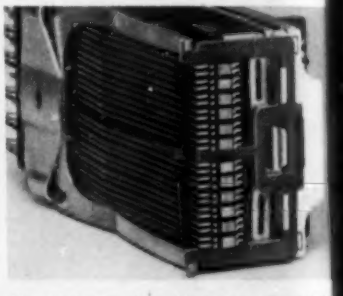


New wire spring relay. Older relays had flat metal springs and 70 parts to be handled, compared with 12 in the new model. Relays operated by means of an electromagnet which responds to high-speed pulses.

In a split second, relays, which are high-speed switches, set up dial telephone connections. Then they are off to direct the next call. Yet even this speed is too slow for Bell Laboratories scientists in quest of still faster switching.

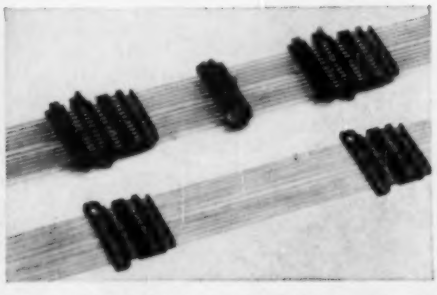
Scientists and engineers devised a new relay – the wire spring relay – and worked out the production problem with Western Electric, manufacturing unit of the Bell System. This is twice as fast, uses less power and costs less to make and maintain.

With speedier relays, switching can be done with less equipment . . . and calls go through faster. The wire spring relay is a practical example of how Bell Telephone Laboratories and Western Electric pool their skills to improve telephone service while keeping its cost down.



New relays must be able to operate one billion times—equal to once-a-second for 30 years. Employing a sound recorder as a precision vibrator, Bell scientists learned to evaluate the effect of sideways motion on relay life. Such rubbing motion is limited to one-thousandth of an inch in the new relays.

Dynamic Fluxmeter, developed by Bell Laboratories, indicates flux build-up in intervals of 25 millionths of a second. Precise information like this was essential to higher speed operation.



Relay springs as they come from Western Electric molding machine, before being cut apart for use. Molding technique saves time and money . . . makes possible the maintenance of precise adjustment.

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IMPROVING TELEPHONE SERVICE FOR AMERICA PROVIDES CAREERS FOR CREATIVE MEN IN SCIENTIFIC AND TECHNICAL FIELDS

Thermogalvanic Potentials

II. Nickel in Neutral Sulfate Solution[1]

DODD S. CARR[2] AND CHARLES F. BONILLA[3]

The Johns Hopkins University, Baltimore, Maryland

ABSTRACT

Thermogalvanic corrosion is a form of galvanic action in which metal dissolves from one surface and deposits on another as the result of a temperature difference between the two surfaces. An apparatus was constructed for measuring the thermogalvanic potential developed by carefully purified nickel powder in several concentrations of neutral nickel sulfate solution under temperature differentials up to 100°C.

Reproducible values of the thermodynamic potential were obtained, and were found to vary more or less linearly with temperature difference and exponentially with nickel concentration. The hotter nickel surface was always negative with respect to the colder surface, thus having a tendency to corrode anodically. Under average conditions the thermogalvanic potential developed was about 0.89 millivolts per °C.

The standard potential of the nickel electrode was computed from isothermal measurements against a calomel electrode, and found to be approximately −0.232 volt on the normal hydrogen scale.

INTRODUCTION

Corrosion of the common structural metals results in heavy financial losses each year, and a thorough study of its causes must be made in order to find satisfactory remedies. Among the causes of corrosion is the effect of differential heating. Thermogalvanic corrosion, as this type is called, is a form of galvanic action in which different metal areas develop different solution potentials, causing metal to dissolve from one surface and deposit on another as a result of a temperature difference. An example of this type of corrosion was described by Maude (2), in which a copper steam coil used to boil hydrochloric acid was found to be destroyed rapidly due to a temperature gradient in the coil, whereas test specimens at the same absolute temperature lasted much longer.

The mechanism of a thermogalvanic cell is comparable to that of a metallic differential thermocouple, the intermediate metallic element being replaced by an electrolytically conducting solution. At the electrodes the passage of current is accompanied by a Peltier type of heat effect, as well as by the transfer of electrode material, while in the temperature gradients the passage of current is accompanied by Thomson heat effects. Metallic conduction across the junction is replaced by electrode reactions which are the reverse of each other, the oxidizing agent which is reduced at the cathode being regenerated at the anode. Thermogalvanic corrosion can proceed indefinitely if not prevented by such factors as the formation of insoluble films.

Early attempts to determine the thermogalvanic potential of nickel were unsuccessful because the unstable nature of the nickel surfaces tested made reproducible results impossible. It was thus the purpose of the present investigation to prepare reproducible nickel electrodes and to measure their thermogalvanic effect. For simplicity, a C.P. nickel sulfate electrolyte was employed. It was also decided to obtain the standard electrode potential of nickel as a check simultaneously on the electrodes employed in the thermogalvanic measurements and on the literature values for this quantity.

A summary of previous thermocell investigations is presented in Table I, covering the period from 1825 to 1950. It begins with the original measurements of Walcker (3) on the direction of the current when a hot and a cold platinum electrode are immersed in an electrolyte at room temperature and concludes with the measurements by Uhlig and Noss (31) of the potentials set up by thermal gradients in iron immersed in sodium chloride solutions.

The first systematic tabulation of the single electrode potentials of the elements was made in 1900, when a careful review of all data then existing was presented by Wilsmore (32). Table II is a summary of the deposition, normal, and standard electrode potentials of nickel that have been published since

[1] Manuscript received December 18, 1951. This paper prepared for delivery before the Detroit Meeting, October 9 to 12, 1951. The first article in this series dealt with the silver chloride thermogalvanic cell and thermodynamic aspects of thermogalvanic cells (1). The authors have kindly consented to a delay in publication so that this paper may be published in the special Theoretical Electrochemistry Issue.

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1900. Since much of the work on this subject in the past involved no special precautions with respect to temperature control, purity of materials and freedom from dissolved oxygen, agreement is far from perfect among the different authors.

TABLE I. *Summary of previous thermocell investigations*

Author	Reference	Year	Nature of investigation
Walcker, A.	(3)	1825	Determined current direction when a hot and a cold Pt electrode were immersed in an electrolyte at room temperature.
Faraday, M.	(4)	1840	Determined current direction when electrolyte was heated with electrodes remaining at same temperature.
Wild, H.	(5)	1858	Studied thermoelectric force developed between unlike solutions.
Mathiessen, A.	(6)	1858	Studied thermoelectric force developed by unlike metals.
Becquerel, E.	(7)	1873	Studied thermoelectric force developed by unlike metals.
Bouty, E.	(8)	1880	Measured thermocells of the type metal-salt solution-metal.
Gore, G.	(9)	1884	Investigated thermocells composed of many metals and electrolytes.
Czapski, S.	(10)	1884	Studied thermocells of insoluble Hg_2Cl_2 and AgCl in metal chloride solutions.
Gockel, A.	(11)	1885	Measured many metallic thermocells under gradients of 0°–40°C. Negative results obtained with nickel strip in $NiCl_2$ solution.
Ebeling, A.	(12)	1887	Copper and zinc thermocells with sulfate and nitrate electrolytes.
Brander, M.	(13)	1888	Studied various thermocells.
Chroustchoff, P., and Sitnikoff, A.	(14)	1889	Measured calomel thermocell and silver-silver chloride.
Nernst, W.	(15)	1889	Used calomel thermocells with HCl, NaOH, and LiCl electrolytes.
Carhart, H. S.	(16)	1893	Measured calomel thermocell and $Ni\text{-}NiSO_4\text{-}CuSO_4\text{-}Cu$ thermocell.
Ostwald, W.	(17)	1893	Discussed theory of thermocells.
Hagenbach, A.	(18)	1894	Obtained unstable values for thermal emf of a nickel thermocell.
Coggeshall, G. W.	(19)	1895	Determined effect of heating and cooling electrodes on emf of calomel thermocell.
Hagenbach, A.	(20)	1896	Found that dilution of electrolyte diminished emf of amalgam thermocells.
Richards, T. W., and Lewis, G. N.	(21)	1897	Studied calomel thermocells with various supernatant liquids.
Benedicks, C.	(22)	1925	Described "action of the hot wall" and resultant pitting of metal.
Eastman, E. D.	(23)	1926	Thermodynamics of thermocells discussed for nonisothermal systems.
Eastman, E. D.	(24)	1928	Gave expression for Soret Coefficients calculated from limited thermogalvanic data.
Eastman, E. D.	(24)	1928	Discussed entropy calculations by means of thermocells.
Clark, W. M.	(25)	1928	Thought thermocells were unimportant since they were not in thermal equilibrium.
Bigalke, I.	(26)	1931	Studied silver thermocell using scraped silver electrodes.
Wesley, W. A., *et al.*	(27)	1932	Investigated thermogalvanic corrosion of nickel in milk.
Maude, A. H.	(2)	1943	Ascribed failure of copper tubing to local temperature differences and not absolute temperature.
Berry, N. E.	(28)	1946	Measured thermogalvanic corrosion in an acid sulfate $Cu\text{-}Cu^{++}$ cell with Cu electrodes maintained at a temperature differential of 150°F.
Buffington, R. M.	(29)	1947	Dealt with thermogalvanic corrosion from thermodynamic point of view.
Levin, H., and Bonilla, C. F.	(1)	1949	Investigated Ag/AgCl/Ag thermocell from thermodynamic standpoint.
Tyrrell, H. J. V., and Hollis, G. L.	(30)	1949	Measured thermal diffusion potentials of Ag-AgCl and Ag-AgBr electrodes in several electrolytes.
Uhlig, H. H., and Noss, O. F. Jr.	(31)	1950	Measured potentials set up by thermal gradients in iron immersed in NaCl solutions.

Apparatus and Procedure

The final form of thermogalvanic cell employed was adapted from the design of Haring and Vanden Bosche (50) by using the curved connecting arm as suggested by Schoch (43) for preventing mixing by convection. Prior designs of thermogalvanic cells which were examined employed solid nickel in the form of wire or strip but failed to give reproducible potential differences, in spite of annealing to remove residual strains and reduction with hydrogen to remove oxide films. The anticipated difficulty of keeping the prepared metal out of all contact with air discouraged further attempts along these lines. The relative ease with which reproducible electrode potentials could be obtained with powdered nickel

in the thermogalvanic cell finally adopted was the reason for its use. A sample of stabilized nickel powder (54) finer than 100 mesh was purified by vacuum evaporation of the residual mercury at 400°C, reduction with hydrogen for 30 minutes at 450° to 500°C, and subsequent evacuation at the same temperature to remove occluded hydrogen.

TABLE II. *Summary of electrode potentials of nickel calculated from observed values*
(Based on normal hydrogen electrode = 0.000 volts)

Investigator	Reference	Electrode potential, volts			Remarks
		Deposition	Normal	Standard	
Neumann, B.	(33)		−0.228		Ni—plated on Ni amalgam—in 1.0*N* $NiSO_4$
Küster, F. W.	(34)	−0.517			Cathodically polarized Ni in 1.0*N* $NiSO_4$
Pfanhauser, W.	(35)		−0.218		Ni—not exposed to air—in 1.0*N* $NiSO_4$
Siemens, A.	(36)		−0.236		Oxygen-free Ni electrode in 2.0*N* $NiSO_4$
St. Labendzinski	(37)				Unable to prepare satisfactory electrodes
Bonsdorff, W.	(38)				Unable to reproduce results
Euler, H.	(39)		−0.155		Etched Ni immersed in 1.0*N* $NiSO_4$
Muthmann, W., and Frauenberger, P.	(40)	−0.603			Ni—polarized in distilled H_2O—in 1.0*N* $NiSO_4$
Coffetti, G., and Foerster, F.	(41)	−0.60			Electrolytic deposition from $NiSO_4$
Thompson, M. deK., and Sage, M. W.	(42)	−0.395			Spongy Ni in neutral molal $NiSO_4$
Schoch, E. P.	(43)		−0.170		Ni wires—heated in N_2 atm—in 1.0*N* $NiSO_4$
Schoch, E. P.	(43)		−0.210		Powdered Ni in 1.0*N* $NiSO_4$
Schweitzer, A.	(44)		−0.279		Pulverized Ni in neutral 1*N* $NiSO_4$ satd. with H_2
Schweitzer, A.	(44)		−0.300		Ni strip in neutral 1*N* $NiSO_4$ satd. with H_2
Schildbach, R.	(45)		−0.223		Powdered Ni in 1.0*N* $NiSO_4$ in atm of N_2
Smits, A., and de Bruyn, L.	(46)		−0.170		Ni wire in boiled-out 1.0*N* $NiSO_4$
Dhar, N. R.	(47)		−0.263		Irreversible Ni electrodes in KCl solutions
Glasstone, S.	(48)	−0.32			Ni deposition on Cu from 1.0*N* $NiSO_4$
Murata, K.	(49)			−0.250	Powdered Ni—by reduction of Ni oxide—in 0.05*M* and 0.005*M* $NiSO_4$ satd. with H_2
Haring, M. M., and Vanden Bosche, E. G.	(50)			−0.231	Powdered Ni in air-free 0.05 to 0.15*M* $NiSO_4$ (25°C)
Colombier, L.	(51)			−0.227	Solid, electrolytic and reduced Ni oxide—free of air contact—in out-gassed 1.0*N* $NiSO_4$ (20°C)
Kurbatov, V. Y., and Myshkovskiĭ, P. P.	(52)			−0.23	Potential measured in presence of Na^+ and $SO^{=}_4$
Scarpa, O.	(53)			−0.17	From emergence energy of electron
Carr, D. S., and Bonilla, C. F.	(Authors)			−0.232	Powdered Ni in out-gassed 0.1, 0.01 and 0.001*M* $NiSO_4$ (25°C)

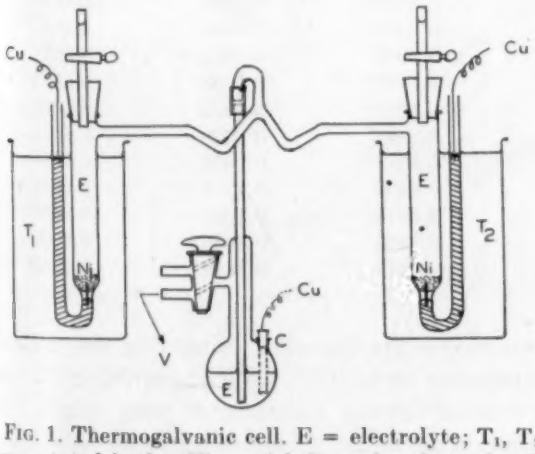

FIG. 1. Thermogalvanic cell. E = electrolyte; T_1, T_2 = thermostated baths; Ni = nickel powder electrode; C = calomel electrode; Cu = copper wire; V = vacuum.

After the nickel cooled under vacuum, direct contact with air was prevented by a liquid seal of out-gassed nickel sulfate solution of the desired composition, which was transferred into the evacuated chamber containing the nickel powder through an evacuated tee-joint. The solutions employed were made from recrystallized reagent grade $NiSO_4 \cdot 6H_2O$ dissolved in distilled water. The electrodes consisted of the powdered nickel lying on the bottom of vertical 2 cm Pyrex glass tubes 17 cm long, with a fine platinum wire sealed through the bottom and with mercury-filled sidearms (Fig. 1). A connecting tube of 8 mm Pyrex glass tubing was curved downward and connected the two electrodes with a 200 ml reservoir of electrolyte fitted with a two-way stopcock for out-gassing the solution by evacuation.

One of the electrodes was maintained at 0°C by ice in a Dewar flask or at 30° to 100°C in 5° intervals by means of an oil bath. Both baths were thermo-

TABLE III. *Observed thermogalvanic potentials of nickel in 0.01M $NiSO_4 \cdot 6H_2O$ with cold electrode at 30.0°, 35.0°, and 40.0°C and copper leads*

(Hot electrode always negative with respect to cold electrode)

Temperature difference between electrodes	Potential difference between electrodes, mv				
	Cold electrode at 30.0 °C	Cold electrode at 35.0°C	Cold electrode at 40.0°C	Calculated by difference	
				30–35°	35–40°
0.0°C	0.0	0.0	0.0	4.5	4.4
5.0	04.5	04.4	04.7	4.4	3.8
10.0	08.8	08.5	08.8	4.5	4.2
15.0	13.0	13.0	13.1	3.9	4.4
20.0	16.9	17.5	17.0	4.0	5.0
25.0	21.5	22.0	21.5	3.8	4.5
30.0	25.8	26.0	25.8	3.9	4.9
35.0	29.9	30.7	30.6	3.8	4.4
40.0	34.5	35.0	35.1	4.3	4.4
45.0	39.3	39.5	40.0	4.3	4.6
50.0	43.8	44.6	44.8	4.0	4.4
55.0	48.6	49.2	49.4	4.1	4.4
60.0	53.3	53.8	54.4	4.3	
65.0	58.1				
70.0	63.2				
Average				4.14	4.45
Standard deviation				0.25	0.25
Average, corrected to nickel leads				4.25	4.56

The experimental procedure consisted of the following steps:

1. The thermogalvanic cell was filled.
2. The cell was allowed to equilibrate at room temperature for three to seven days.
3. The unsymmetrical temperature hump test was carried out with the two electrodes maintained at the same temperature (29, 1).
4. The emf was measured with one electrode at 0.0°C and the other at 30.0°C, until thermal equilibrium had been reached at the electrodes and reproducible potential differences were obtained.
5. The emf was measured with one electrode at 30.0°C and the other electrode at 5° intervals from 30° up to 100°C until reproducible potential differences were obtained at each interval; in addition, this was repeated with the cold electrode at 35° and at 40° with the 0.01*M* electrolyte.
6. The potential difference at room temperature between the nickel electrodes and a saturated calomel electrode was measured.

Experimental Results

The numerical values obtained are given in Table III, IV, and V. Table III shows that for the 0.01 molar electrolyte the effect of varying the electrode temperature up to 10°C, while maintaining the temperature difference constant, is very slight. The maximum deviation for a ten-degree change in electrode temperature was 1.1 mv for a temperature difference of 60°C. Table IV lists the results for a cold electrode temperature of 30°C and electrolyte concentrations of 0.0001 to 1.0*M*. In Table V the potential of a nickel electrode compared to that of a

TABLE IV. *Observed thermogalvanic potential differences in nickel sulfate solution after correction for thermocouple effect of copper leads*

Cold electrode temperature	Hot electrode temperature	Molarity of nickel sulfate electrolyte				
		0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*	1.0 *M*
0.0°	30.0°	0.0092 v	0.0132 v	0.0155 v	0.0211 v	0.0252 v
30.0	30.0	0.0000	0.0000	0.0000	0.0000	0.0000
30.0	35.0	—	0.0036	0.0046	0.0045	0.0044
30.0	40.0	—	0.0072	0.0090	0.0090	0.0090
30.0	45.0	—	0.0113	0.0133	0.0136	0.0135
30.0	50.0	0.0124	0.0154	0.0173	0.0183	0.0182
30.0	55.0	0.0156	0.0196	0.0221	0.0231	0.0227
30.0	60.0	0.0187	0.0238	0.0265	0.0277	0.0274
30.0	65.0	0.0238	0.0281	0.0307	0.0323	0.0319
30.0	70.0	0.0279	0.0320	0.0354	0.0372	0.0367
30.0	75.0	0.0310	0.0368	0.0403	0.0420	0.0411
30.0	80.0	0.0346	0.0411	0.0449	0.0466	0.0461
30.0	85.0	0.0377	0.0457	0.0498	0.0514	0.0511
30.0	90.0	0.0413	0.0503	0.0546	0.0564	0.0560
30.0	95.0	0.0460	0.0550	0.0596	0.0615	0.0609
30.0	100.0	0.0511	0.0596	0.0648	0.0668	0.0660

stated to within 0.1°C of the desired temperature by means of electric stirrers and mercury-toluene regulators controlling immersion heaters. Calibrated thermometers graduated in 0.1°C were used to measure the electrode temperatures. The potential difference between the hot and cold electrodes was measured with a Leeds and Northrup student-type potentiometer and a Fisher type F reflecting galvanometer.

saturated calomel electrode at 30°C is given, as computed from Tabe IV and the potentials in Table VI observed vs. a calomel electrode near 30°C. In Table V the expected potentials against a normal hydrogen electrode at 30°C are also listed, based on the generally accepted value of +0.2424 volt for the potential at 30°C of the saturated calomel vs. the normal hydrogen electrode.

For the 0.0001*M* solution it was not possible to obtain reproducible potential differences when the temperature difference between the electrodes was less than 20°C. Since copper wire leads were used to the mercury sidearms, the observed potential differences were all corrected for the effects of the resulting copper-nickel thermocouple before entering in Tables IV and V. This correction amounted to −2.24 mv per 100°C (55), directed toward increasing the absolute value of the observed potentials. These baths were well stirred, so that no temperature differential is believed to have existed across the mercury column.

The potential difference between the hot and the cold electrode was substantially a linear function of the temperature difference, as seen in Fig. 2. For the more dilute electrolytes there was a slight deviation from linearity at 55° to 65°C, for which no explanation is apparent. In addition, on extrapolation the curves increasingly miss the origin the more dilute the

TABLE V. *Potential of the nickel electrode in neutral nickel sulfate solution at various temperatures vs. the normal hydrogen and the saturated calomel electrodes at 30°C*
(Volts)

Temp °C	0.0001 *M*		0.001 *M*		0.01 *M*		0.1 *M*		1.0 *M*	
	E_H	$E_{cal.}$	E_H	$E_{cal.}$	E_H	$E_{cal.}$	E_H	$E_{cal.}$	E_H	$E_{cal.}$
0.0	−.342	−.585	−.320	−.562	−.294	−.537	−.268	−.511	−.237	−.479
30.0	−.351	−.594	−.333	−.575	−.310	−.553	−.289	−.532	−.262	−.504
35.0	—	—	−.337	−.579	−.315	−.558	−.294	−.537	−.266	−.508
40.0	—	—	−.340	−.582	−.319	−.562	−.298	−.541	−.271	−.513
45.0	—	—	−.344	−.586	−.323	−.566	−.303	−.546	−.276	−.518
50.0	−.363	−.606	−.348	−.590	−.327	−.570	−.307	−.550	−.280	−.522
55.0	−.367	−.610	−.353	−.595	−.332	−.575	−.312	−.555	−.285	−.527
60.0	−.370	−.613	−.357	−.599	−.337	−.580	−.317	−.560	−.289	−.531
65.0	−.375	−.618	−.361	−.603	−.341	−.584	−.321	−.564	−.294	−.536
70.0	−.379	−.622	−.365	−.607	−.345	−.588	−.326	−.569	−.299	−.541
75.0	−.382	−.625	−.370	−.612	−.350	−.593	−.331	−.574	−.303	−.545
80.0	−.386	−.629	−.374	−.616	−.355	−.598	−.336	−.579	−.308	−.550
85.0	−.389	−.632	−.379	−.621	−.360	−.603	−.340	−.583	−.313	−.555
90.0	−.392	−.635	−.383	−.625	−.365	−.608	−.345	−.588	−.318	−.560
95.0	−.397	−.640	−.388	−.630	−.370	−.613	−.351	−.594	−.323	−.565
100.0	−.402	−.645	−.393	−.635	−.375	−.618	−.356	−.599	−.328	−.570

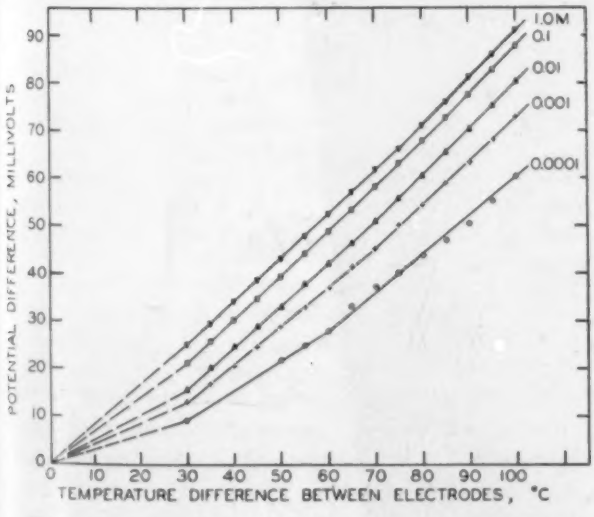

FIG. 2. Thermogalvanic potential of a nickel electrode at 0°C with respect to a warmer one vs. temperature difference and molarity of neutral $NiSO_4$ electrolyte (calculated from Table IV).

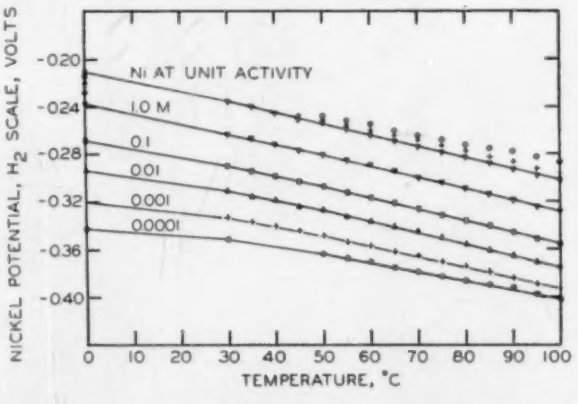

FIG. 3. Potential of the nickel electrode with respect to the normal hydrogen electrode at 30°C vs. temperature and concentration of the $NiSO_4$ electrolyte.

electrolyte. The average slope of the intermediate portions of the curves of Fig. 2 is approximately 0.89 mv per °C. The potentials vs. the normal

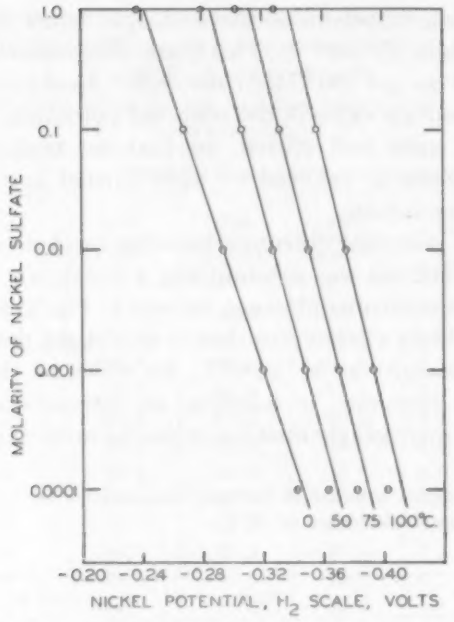

FIG. 4. Potential of the nickel electrode with respect to the normal hydrogen electrode at 30°C vs. the logarithm of the molarity.

galvanic potentials were reversible. The first step was to identify the electrode reactions and to prove that high and low temperature reactions were the reverse of each other as revealed by the electrochemical equivalent of the metal plated out during short-circuiting, particularly as determined by plating tests with a coulometer. Short-circuiting an earlier type of cell used in this study resulted in pitting of the hot electrode, but the cells containing purified nickel powder were not short-circuited because of the problem of observing any transfer of metal and the danger of polarization of the electrodes. The second step was to test whether the electrodes operated reversibly, as shown by isothermal tests after preliminary equilibration of the cell. The isothermal potential should be less than several tenths of a millivolt. If a change in potential of 0.1 millivolt was sufficient to reverse the direction of the galvanometer deflection—and therefore the direction of the current in the cell—the reversibility of the electrode reactions was deemed to be established. All the types of cells examined prior to those

TABLE VI. *Calculation of standard nickel electrode potential, E, at 25°C from isothermal emf vs. saturated calomel*

$NiSO_4$ Molarity, M	0.0001	0.001	0.01	0.1	1.0
Temperature, t, °C	30.2	30.1	29.9	29.5	31.6
Observed emf vs. satd. calomel, mv	−593.5	−575.2	−553.0	−532.2	−506.4
dE_{ai}/dt, mv/°C	−0.42	−0.56	−0.70	−0.80	−0.88
dE_{H_2Cl}/dt, mv/°C	+0.20	+0.20	+0.20	+0.20	+0.20
emf vs. satd. calomel at 25°C, mv	−590.4	−571.3	−548.6	−527.7	−499.2
emf vs. N Hydrogen at 25°C, mv	−344.6	−325.5	−302.8	−281.9	−253.4
Based on activity coefficient of $ZnSO_4$ at 25°C:*					
Mean activity coefficient, γ		0.734	0.387	0.148	0.044
E at 25°C, v		−0.2328	−0.2315	−0.2278	−0.2133
Based on activity coefficient of $NiSO_4$ at 25°C:**					
Mean activity coefficient, γ				0.150	0.0425
E at 25°C, v				−0.2280	−0.2131
Based on Debye-Hückel Limiting Law:†					
Mean activity coefficient, γ	0.911	0.756	0.458	0.1625	0.0440
E at 25°C, v	−0.2250	−0.2333	−0.2337	−0.229	−0.2133

* Reference (56), p. 236.
** ROBINSON AND HARNED, *Chem. Revs.*, **28**, 419 (1941).
† Reference (56), p. 146.

hydrogen electrode are plotted against temperature in Fig. 3, and cross-plotted against the logarithm of the concentration in Fig. 4 for comparison and interpolation.

Reversibility of Open-Circuit Potentials

Three steps were outlined by Buffington (29) to determine in specific cases whether or not thermal

containing powdered nickel failed to pass the isothermal test at room temperature and were consequently rejected, whereas cells containing powdered nickel were satisfactory. The third step was to test the reversibility of the electrolytic conduction by setting up an unsymmetrical temperature hump in a portion of the electrolytic path with the electrodes at the same temperature and watching for deflection of

the galvanometer. This test was also applied with the electrodes at widely differing temperatures and the potentiometer balanced, and no galvanometer deflections were detected. However, the test is most accurate with the electrodes at the same temperature.

Standard Electrode Potential of Nickel

The standard electrode potential of nickel on the normal hydrogen scale is the potential of a nickel electrode in an electrolyte of unit nickel ion activity with respect to a 1*N* hydrogen electrode, without liquid junction potentials. It can be obtained most accurately from a cell without a liquid junction, such as the cell $Ni/NiSO_4(M)/Hg_2SO_4/Hg$ used by Haring and Vanden Bosche (50), by correcting the observed potential by the term $(RT/\mathbf{F})\ln(\gamma M)$, where the activity coefficient γ is the mean activity coefficient of the Ni and SO_4 ions (56).

However, approximate values of the standard electrode potential can also be calculated from a cell with a liquid junction, such as the Ni-HgCl cell employed in this study. The junction potential must be neglected (or estimated) and the observed potential corrected by the term $(RT/n\mathbf{F})\ln(\gamma_+ M)$, where γ_+ is the activity coefficient of the Ni ions alone. Such a calculation has been outlined in Table VI. Rather good agreement is observed between the 0.001*M* and 0.01*M* electrolytes. At the higher concentrations more error is probably introduced by neglect of the liquid junction and by assuming that the activity of the nickel and sulfate ions is the same. The lowest concentration is possibly in error for other reasons, as previously suggested. The final average value of the standard potential of nickel would seem to be about −0.232 volts, in excellent agreement with Haring and Vanden Bosche's value of −0.231 volt.

Accuracy of Data

The observed potential differences between the hot and cold nickel electrodes were rounded off to the nearest tenth of a millivolt and are all believed to be accurate to within 0.5 millivolt, with the exception of the 0.0001*M* nickel sulfate cell, for which they are believed accurate to within 1 millivolt. A quantitative estimate of the reliability of the thermogalvanic potentials may be obtained from the data in Table III. The difference between a value in the first column and the preceding one in the second column should be the thermogalvanic potential for a hot electrode at 35°C and a cold one at 30°C. The 13 such values are shown in Table III, and give a mean of 4.14 mv with a standard deviation of 0.25 mv. Similarly, from the second and third columns the cell with electrodes at 40° and 35°C has a mean of 4.45 mv, again with a standard deviation of 0.25 mv. Since each of these voltages is in fact the difference between the observed voltages of two complete cells, the standard deviation of 0.25 mv is the standard deviation of the difference between two quantities having, presumably, the same standard deviation. The standard deviation of each thermogalvanic potential is thus only 0.707 x 0.25 = 0.18 mv.

Acknowledgment

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REFERENCES

1. H. Levin, *Dissertation*, Department of Chemical Engineering, The Johns Hopkins University (1949); H. Levin and C. F. Bonilla, *J. Electrochem. Soc.*, **98**, 388 (1951).
2. A. H. Maude, *Trans. Am. Inst. Chem. Eng.*, **39**, 752 (1943).
3. Adolph Walcker, *Pogg. Ann.*, **4**, 327 (1825).
4. M. Faraday, *Exp. Res. Ser.*, **17**, 1932 (1840).
5. H. Wild, *Pogg. Ann.*, **103**, 353 (1858).
6. A. Mathiessen, *Pogg. Ann.*, **103**, 412 (1858).
7. E. Becquerel, *Ann. chim. et phys.*, (4) **8**, 192 (1873).
8. E. Bouty, *J. phys.*, **9**, 229 (1880); *Compt. rend.*, **90**, 919 (1880).
9. G. Gore, *Proc. Roy. Soc.* (*London*), **37**, 251 (1884).
10. S. Czapski, *Wied. Ann.*, **21**, 209 (1884).
11. A. Gockel, *Wied. Ann.*, **24**, 618 (1885).
12. A. Ebeling, *Wied. Ann.*, **30**, 530 (1887).
13. M. Brander, *Akad. Abhandlg. Helsingfors* (1888).
14. P. Chroustchoff and A. Sitnikoff, *Compt. rend.*, **108**, 937 (1889).
15. W. Nernst, *Z. physik. Chem.*, **4**, 169 (1889).
16. H. S. Carhart, *Am. J. Sci.*, **46**, 66 (1893).
17. W. Ostwald, "Lehrbuch der Allgemeine Chemie," Vol. 2, Engelmann, Leipzig (1893).
18. A. Hagenbach, *Wied. Ann.*, **53**, 447 (1894).
19. G. W. Coggeshall, *Z. physik. Chem.*, **17**, 62 (1895).
20. A. Hagenbach, *Wied. Ann.*, **58**, 21 (1896).
21. T. W. Richards and G. N. Lewis, *Proc. Am. Acad.*, **34**, 87 (1898); *Z. physik. Chem.*, **28**, 1 (1899).
22. C. Benedicks, *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 597 (1925).
23. E. D. Eastman, *J. Am. Chem. Soc.*, **48**, 1482 (1926).
24. E. D. Eastman, *J. Am. Chem. Soc.*, **50**, 283, 292 (1928).
25. W. M. Clark, "The Determination of Hydrogen Ions," 3rd ed., p. 450, Williams and Wilkins, Baltimore, Md. (1928).
26. I. Bigalke, *Z. physik. Chem.*, **154**, 128 (1931).
27. W. A. Wesley, H. A. Trebler, and F. L. LaQue, *Trans. Am. Electrochem. Soc.*, **61**, 459 (1932).
28. N. E. Berry, *Corrosion*, **2**, 261 (1946).
29. R. M. Buffington, *Corrosion*, **3**, 613 (1947).

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30. H. J. V. Tyrrell and G. L. Hollis, *Trans. Faraday Soc.*, **45**, 411 (1949).
31. H. H. Uhlig and O. F. Noss, Jr., *Corrosion*, **6**, 140 (1950).
32. N. T. M. Wilsmore, *Z. physik. Chem.*, **35**, 316 (1900).
33. B. Neumann, *Z. physik. Chem.*, **14**, 215 (1894).
34. F. W. Küster, *Z. Elektrochem.*, **7**, 258 (1900).
35. W. Pfanhauser, *Z. Elektrochem.*, **7**, 698 (1900).
36. A. Siemens, *Z. anorg. allgem. Chem.*, **41**, 264 (1904).
37. St. Labendzinski and R. Abegg, *Z. Elecktrochem.*, **10**, 77 (1904).
38. W. Bonsdorff, *Akad. Abhandlg. Helsingfors*, p. 17 (1904).
39. H. Euler, *Z. anorg. Chem.*, **41**, 93 (1904); *Jahrb. Elektrochem.*, **11**, 354 (1904).
40. W. Muthmann and F. Frauenberger, *Sitz. Bayr. Akad. Wiss.*, **34**, 201 (1904).
41. G. Coffetti and F. Foerster, *Ber.*, **38**, 2937 (1905); *Jahrb. Elektrochem.*, **12**, 481 (1905).
42. M. deK. Thompson and M. W. Sage, *J. Am. Chem. Soc.*, **30**, 717 (1908).
43. E. P. Schoch, *Am. Chem. J.*, **41**, 208 (1909).
44. A. Schweitzer, *Z. Elektrochem.*, **15**, 609 (1909).
45. R. Schildbach, *Z. Elektrochem.*, **16**, 977 (1910).
46. A. Smits and L. de Bruyn, *Proc. Acad. Sci. Amsterdam*, **20**, 394 (1918).
47. N. R. Dhar, *Z. anorg. allgem. Chem.*, **118**, 78 (1921).
48. S. Glasstone, *J. Chem. Soc.*, **48**, 2892 (1926).
49. K. Murata, *Bull. Chem. Soc. Japan*, **3**, 57 (1928); *Tech. Repts. Tôhoku Imp. Univ.*, **7**, 171 (1927).
50. M. M. Haring and E. G. Vanden Bosche, *J. Phys. Chem.*, **33**, 161 (1929).
51. L. Colombier, *Compt. rend.*, **199**, 273 (1934).
52. V. Y. Kurbatov and P. P. Myshkovskiĭ, *Khim-Tekh. Inst.*, **1938**, No. 6, 108; *Khim. Referat. Zhur.*, **1**, No. 11–12, 10 (1938).
53. O. Scarpa, *Atti accad., Italia, Rend. classe sci. fis., mat. nat.*, (7) **1**, 204 (1939).
54. O. G. Bennett, U. S. Pat. 2,487,632, Nov. 8, 1949; *Chem. Abstracts*, **44**, 1710e (1950).
55. American Institute of Physics, "Temperature," p. 1309, Reinhold Publishing Corp., New York (1941).
56. S. Glasstone, "Introduction to Electrochemistry," pp. 139, 236, D. Van Nostrand Co., New York (1942).

Ion Association of 2-1 Salts in Methanol[1]

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ABSTRACT

Conductance curves for many 2-1 salts in methanol (and other solvents of intermediate dielectric constant) approximate linearity over a fairly wide range of concentration. This linear region is an inflection range, produced by a combination of decreasing mobility ($c^{\frac{1}{2}}$ terms) and decreasing number of free ions (c terms) with increasing concentration. It may, therefore, not be used for extrapolation to Λ_0. Assuming stepwise association: (a), $A' + B^{++} \rightleftharpoons AB^+$; ($b$), $AB^+ + A' \rightleftharpoons BA_2$, a method of successive approximations is derived by which Λ_0, k_1 and k_2 can be calculated from conductance data.

Introduction

Conductance curves for typical 2-1 salts in water (1) at low concentrations approach the slope predicted by the Debye-Hückel-Onsager theory; the deviations, which can be summarized by terms in c and c log c, presumably arise from mathematical approximations made in the derivation. In solvents of lower dielectric constant, a deceptive approach to linearity of the $\Lambda - c^{\frac{1}{2}}$ curves is observed. The slope of the apparently linear section of the curve is, however, considerably larger than the theoretical value; nevertheless, some authors have extrapolated linearly along this region of the curve in the hope of obtaining Λ_0. One author has gone to the extreme of calculating "effective dielectric constants" from these slopes. Now it is known that 1-1 salts exhibit an inflection region in solvents of low dielectric constant, due to ion association (2); it, therefore, seems worth while to consider the 2-1 case from this point of view.

When the two charges of the cation are near the terminal atoms of a chain, the electrolyte shows association of anion to one end of the cation in methanol (3, 4). This result suggests that the initial association in the case of cations such as Mg^{++}, where both charges are concentrated on one atom, would be

$$Mg^{++} + Cl' \rightleftharpoons (MgCl)^+.$$

As concentration is further increased, the positive $MgCl^+$ complex might then combine with an additional anion to give the neutral $Cl' \cdot Mg^{++} \cdot Cl'$ cluster, because 1-1 salts are known to associate in methanol. In other words, at very low concentrations, the electrolyte would behave as a normal 2-1 salt, and at intermediate concentrations as a mixture of 1-1 and 2-1 salts. These equilibria, together with the usual $c^{\frac{1}{2}}$ mobility terms, would lead to an inflection point in the $\Lambda - c^{\frac{1}{2}}$ curve, which would produce a range in which the curve was nearly linear (where it was changing from concave-up to concave-down); it is this pseudo-linear region which has erroneously been used for extrapolation.

The purpose of this paper is to present a method of analyzing conductance data for 2-1 salts, on the assumption that the equilibria[2]

$$AB^+ + A' \rightleftharpoons A_2B \qquad \text{(I)}$$

$$A' + B^{++} \rightleftharpoons AB^+ \qquad \text{(II)}$$

control the properties. Briefly described, the method is a cycle of successive approximations, which leads to values of Λ_0 and of k_1 and k_2, the constants describing the associations (I) and (II). It should be emphasized that the symbols AB^+ and BA_2 represent structures in which the ions B^{++} and A' retain their identities as ions; the clusters are assumed to be stabilized against thermal impact solely by electrostatic attraction. The situation in which covalent bonds are involved requires a different approach (5–7).

Method

If we assume association equilibria (I) and (II), three conducting species A', B^{++}, and AB^+ are present in the solution. The equivalent conductance Λ, defined as $1000\ \kappa/c$, where κ is specific conductance and c is stoichiometric concentration (equivalents per liter), is, therefore, the sum of three terms:

$$\Lambda = \gamma_1\lambda_1 + 2\gamma_2\lambda_2 + \gamma_3\lambda_3 \qquad \text{(III)}$$

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[2] The equations are deliberately written in the reverse of the conventional direction in order to emphasize the fact that the primary step is *association of ions* rather than *dissociation of molecules*. The writers prefer therefore to call the k's "reciprocal association constants" instead of "dissociation constants."

where the λ's are the single ion conductances and the γ's represent the fractions of salt present in the various species:

$$c\gamma_1 = [A'], \quad c\gamma_2 = [B^{++}], \quad c\gamma_3 = [AB^+]. \quad (IV)$$

Here, bracketed quantities refer to moles per liter of the corresponding species; in the limit of zero concentration, $\gamma_1 = 1$, $\gamma_2 = \frac{1}{2}$ and $\gamma_3 = 0$. The condition of electrical neutrality requires that at all concentrations

$$\gamma_1 = 2\gamma_2 + \gamma_3. \quad (V)$$

The formal mass action equations for equilibria (I) and (II) are

$$k_1 = ([AB^+][A']/[A_2B])(f_{AB}f_A/f_{A_2B})$$

and

$$k_2 = ([A'][B^{++}]/[AB^+])(f_Af_B/f_{AB}).$$

In terms of the γ's, these become

$$k_1 = 2c\gamma_1\gamma_2f_1^2/(1 - \gamma_1 - \gamma_3) \quad (VI)$$

and

$$k_2 = c\gamma_1(\gamma_1 - \gamma_3)f_2/2\gamma_3 \quad (VII)$$

where we have set $f_{AB} = f_A = f_1$, $f_B = f_2$ and $f_{A_2B} = 1$, used the neutrality condition (V) to eliminate γ_2 and used the equation

$$\text{Total } [A'] = c = 2[A_2B] + 2[B^{++}] + 2[AB^+]$$

to evaluate the concentration of neutral clusters:

$$[A_2B] = c(1 - 2\gamma_2 - 2\gamma_3)/2. \quad (VIII)$$

The individual λ's of (III) are of the form

$$\lambda_j = \lambda^0_j - \Delta\lambda_j \quad (IX)$$

where λ^0_j is the limiting equivalent conductance of the j-th species, and $\Delta\lambda_j$ is a complicated function (8) of the individual ion concentrations and mobilities.

Equations (III), (VI), and (VII) can be written symbolically as

$$F_1(c, \gamma_1, \gamma_3) = k_1 \quad (VI')$$

$$F_2(c, \gamma_1, \gamma_3) = k_2 \quad (VII')$$

$$\Lambda = \Lambda_0 - \phi(c, \gamma_1, \gamma_3). \quad (III')$$

In principle, our procedure is now simple: we should solve (VI) and (VII) for γ_1 and γ_3 in terms of c, k_1, and k_2 and substitute the result in (III), obtaining

$$\Lambda = \Lambda_0 - \psi(c, k_1, k_2). \quad (III'')$$

Then by substituting conductances at three concentrations in (III″), we would obtain three equations, the solution of which would give us the desired constants Λ_0, k_1, and k_2 which describe the system. Practically, however, this direct attack appears hopeless: the f's are transcendental functions of the γ's, and the Δλ's bring in awkward radicals and cross-products; even without these difficulties, combination of (VI) and (VII) leads immediately to a cubic which would be tedious to solve. We must, therefore, proceed in quite a different fashion.

For the case of bolaform electrolytes (3, 4), where the charges are separated by a number of neutral atoms, the problem was solved by assuming in first approximation that the concentration of neutral BA_2 clusters was negligible at low concentrations. This assumption is equivalent to setting $k_1 = \infty$, and reduces the problem to the fairly simple one of determining two constants, Λ_0 and k_2, from the data. When the two charges are concentrated on one atom, as in the alkaline earths, this simplifying assumption can no longer be made. The open circles of Fig. 1 show the result of applying Fuoss and Edelson's method to data for magnesium chloride (9) in methanol at 20°. (The variable Y is proportional to the x of Ref. 3.) The curve is useless for estimating k_2, although it does give a fairly good value for Λ_0. The absurd negative values for Y suggest the method of improving the calculation: they appear because too large a term was subtracted in Y, and the negative term in Y is a direct consequence of the approximation $[BA_2] = 0$. We, therefore, drop this approximation and approach the problem from a different point of view.

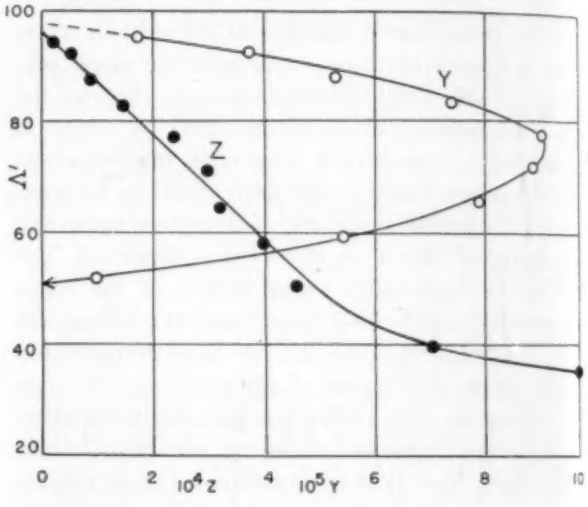

FIG. 1. Y-curve: test of assumption that $k_1 = \infty$. Z-curve: test of equation (XXIX).

If two charges are present on one atom, the local field must be quite intense; we, therefore, assume that the cluster AB^+ is stable in methanol and, to first approximation, treat the salt as if it were a 1-1 electrolyte (AB^+) (A'). By using familiar methods (2), we calculate K from the data in the *intermediate*

range of concentrations, and as our starting approximation, set $K = k_1$. Then with a numerical value for k_1, we can combine equations (III), (VI), and (VII) in such a way that a suitable extrapolation function for Λ_0 and k_2 is obtained; it is the Fuoss and Edelson function, adapted to the more general case. (It should perhaps be mentioned that equilibrium (II) must be the one which controls the approach to $c = 0$, regardless of the simulation of 1-1 behavior in the higher ranges of concentration.) The values of k_1, k_2, and Λ_0 so obtained are all first approximations, of course; it is obviously possible to feed k_2 and Λ_0 back into the equation for k_1 to get a second approximation for k_1, and then to use this value to obtain an improved value of Λ_0 and k_2. We have, however, found that one cycle gives a very good value of Λ_0.

Calculations

The details of the method are best explained by means of a specific example. Before proceeding to this, it will be convenient to collect the coefficients needed to calculate the terms which arise from long range interaction of ions. These can best be given in terms of the ional concentration, which here is explicitly

$$\Gamma = c(\gamma_1 + 4\gamma_2 + \gamma_3) = c(3\gamma_1 - \gamma_3). \quad (X)$$

As the calculation proceeds, successively better approximations will be used for Γ, beginning with the very rough estimate $\Gamma = 2c\Lambda/\Lambda_0$.

For the activity coefficients, we shall use the leading term (10) of the Debye-Hückel equation

$$-\log f_j = 1.283 \times 10^6 z_j^2 \Gamma^{\frac{1}{2}}/(DT)^{\frac{3}{2}} \quad (XI)$$

where z_j is the valence of the corresponding ion.[3]

In calculating the mobility corrections, we shall neglect cross-product terms (8) and treat the mixture as if conductances were additive in mixed salts. (For a qualitative estimate of this approximation, see Fig. 4 and 5 of Ref. 8.) The single ion mobility correction in (IX) is then

$$\Delta\lambda_j = S_j\Gamma^{\frac{1}{2}} \quad (XII)$$

where (11)

$$S_j = \frac{1.970 \times 10^6}{(DT)^{\frac{3}{2}}} \frac{q^*}{1 + \sqrt{q^*}} |z_1 z_2| \lambda_j^0 + \frac{28.98\,|z_j|}{\eta\,(DT)^{\frac{1}{2}}}. \quad (XIII)$$

Here q^* is 0.5 for a 1-1 salt (i.e., in the range where A_2B acts like AB^+ and A') and for a 2-1 salt (i.e., at low concentrations where A_2B acts like $2A'$ and B^{++})

$$q^* = 2/3(1 + \lambda^0_1/\Lambda_0). \quad (XIV)$$

It is convenient to write (XII) in the form

$$\Delta\lambda_j = \Lambda_0\delta_j\Gamma^{\frac{1}{2}} \quad (XV)$$

where $j = 1$, 2, or 3, according to the convention of indices defined in (IV); we shall use the symbols δ_{12} and δ_{13} to mean $(\delta_1 + \delta_2)$ and $(\delta_1 + \delta_3)$, respectively. Thus, for example, at very low concentrations, the limiting law takes the form

$$\Lambda = \Lambda_0(1 - \delta_{12}\Gamma^{\frac{1}{2}}). \quad (XVI)$$

In order to make later equations more compact, we shall use the further abbreviations

$$D_{12} \equiv 1 - \delta_{12}\Gamma^{\frac{1}{2}} \equiv 1/H_{12}. \quad (XVII)$$

The calculation begins with an apparent obstacle: the purpose of the calculation is to obtain Λ_0 (and the k's), but in order to begin the solution, we need a numerical value of Λ_0 in order to estimate the activity and mobility terms. This difficulty is removed when we recall that these terms are essentially correction terms, whose (multiplicative) value approaches unity as the concentration approaches zero. Hence a rough approximation to Λ_0 (e.g., a free hand extrapolation of the $\Lambda - c^{\frac{1}{2}}$ curve) may be used in the first step; after this, the calculation itself provides successively better values for Λ_0.

Another not quite trivial complication must be removed by approximation in order to begin the calculation. If we substitute (IX) in (III), algebraic chaos results, even with neglect of those cross terms which are due to failure of Kohlrausch's law of additive conductance in mixed electrolytes (12). As an initial approximation (which can be corrected in subsequent steps), we shall write the combination of (III), (IX), and (XV) in the form

$$\Lambda = (\gamma_1\,\lambda^0_1 + 2\gamma_2\lambda^0_2 + \gamma_3\lambda^0_3)(1 - \delta_{12}\Gamma^{\frac{1}{2}}) \quad (XVIII)$$

i.e., apply to *all* ions the correction for a 2-1 electrolyte, and justify the factorization by the realization that γ_3 approaches zero as concentration decreases. Using the neutrality condition and the abbreviation (XVII), we then have

$$H_{12}\Lambda = \gamma_1\Lambda_0 - \gamma_3(\lambda^0_2 - \lambda^0_3) \quad (XIX)$$

where

$$\Lambda_0 = \lambda^0_1 + \lambda^0_2. \quad (XX)$$

Applications

Let us now consider a specific example: magnesium chloride in methanol (9) at 20°, where the dielectric constant (13) is 32.35 and the viscosity (14)

[3] In order to avoid confusion, we point out here that Harned and Owen use c_i to represent *moles* per liter of the i-th component, while our symbol c represents *equivalents* per liter of the monovalent constituent.

$\eta = 0.00593$. Using Hartley's value (15) for the conductance of the chloride ion in methanol at 25°, we have λ^0_1 (25°) = 51.3. For temperature changes, it probably is safe to use Walden's rule, whence $\lambda^0_1(20°) = 47.3$, using Maclay's (16) value of 0.00546 for the viscosity at 25°. For λ^0_3, the conductance of the $(MgCl)^+$ ion, we shall use the approximation $\lambda^0_1 = \lambda^0_3$, which is an upper limit for λ^0_3. Changing the value of λ^0_3 does not affect Λ_0 or k_2 very much, but k_1 is sensitive to λ^0_3.

For $MgCl_2$ considered as (MgCl) (Cl), $\Lambda_0 = \lambda^0_1 + \lambda^0_3 = 94.6$. This gives $\delta_{13} = 0.624 + 100.4/\Lambda_0$. We next calculate $z = \alpha\sqrt{c\Lambda}/\Lambda_0^{\frac{3}{4}}$ where $\alpha = \delta_{13}\sqrt{2}$. Using the tabulated (17) F-function, we obtain γ; since we are neglecting γ_2 here, $\gamma = \gamma_1 = \gamma_3$, and

$$k_1 = c\gamma^2 f^2/(1 - \gamma). \qquad \text{(XXI)}$$

The extrapolation plot is constructed in the usual way (2); the points in the concentration range 3×10^{-4} to 2×10^{-3} show some curvature, but can be approximated by a straight line, whose slope (using $\Lambda_0 = 94.6$) gives the preliminary value

$$k_1 = 3.6 \times 10^{-4}.$$

Now if we solve (VI) for γ_3, we have

$$\gamma_3 = (1 - \gamma_1)/(1 + 2cf_1^2\gamma_1/k_1)$$

$$\equiv (1 - \gamma_1)/(1 + \Delta). \qquad \text{(XXII)}$$

As a starting approximation for Δ, we set γ_1 equal to Λ/Λ_0 and $\Gamma = 2c\Lambda/\Lambda_0$ to calculate f_1^2 by (X). Using the corresponding value of Δ, we get a zeroth approximation for Γ:

$$\Gamma^0 = c\left(\frac{3\Lambda}{\Lambda_0} - \frac{1 - \Lambda/\Lambda_0}{1 + \Delta^0}\right). \qquad \text{(XXIII)}$$

In order to obtain the mobility correction (XVII), we use $\Lambda_0 = 98$; i.e., a value somewhat smaller than the 101.6 obtained by linear extrapolation of the inflection region. Then $\lambda^0_2 = 50.7$ and $\delta_{12} = 2.69$. We rearrange the conductance equation (XVIII) after substitution of (V) as follows:

$$\gamma_1 = (H_{12}\Lambda + P)/(\Lambda_0 + P) \qquad \text{(XXIV)}$$

where

$$P = (\lambda^0_2 - \lambda^0_3)/(1 + \Delta). \qquad \text{(XXV)}$$

In (XXV), we use the zeroth approximation for Δ and in (XXIV), set H_{12} equal to $1/(1 - 2.69\sqrt{\Gamma^0})$. The values of γ_1 so obtained are tabulated as γ_1', the first approximation to γ_1. These values are returned to (XXII) to give first Δ' and then γ_3', where the zeroth approximation for f_1^2 is still used, and we now have a good first approximation to Γ:

$$\Gamma' = c(3\gamma_1' - \gamma_3'). \qquad \text{(XXVI)}$$

With this, we compute f_2 by (11), and get a first approximation to f_1^2 for use in calculating Δ'' by the obvious relation $\sqrt{f_2} = f_1^2$.

Next, we rearrange (VII) as follows:

$$\Lambda' = \Lambda_0 - (\Lambda_0/2k_2)Z \qquad \text{(XXVII)}$$

where

$$\Lambda' = \Lambda_0\gamma_1' \qquad \text{(XXVIII)}$$

and

$$Z = c\gamma_1' f_2(2\gamma_1' - 1 + \gamma_1'\Delta''). \qquad \text{(XXIX)}$$

In this form, errors in the choice of the initial value of Λ_0 can no longer cause a singularity at $c = 0$ and the errors in γ_1' affect Z multiplicatively. Since Z vanishes at $c = 0$, a plot of Λ' against Z should approach linearity at small values of c and should extrapolate to a satisfactory value of Λ_0. The slope near $Z = 0$ will give a preliminary value of k_2.

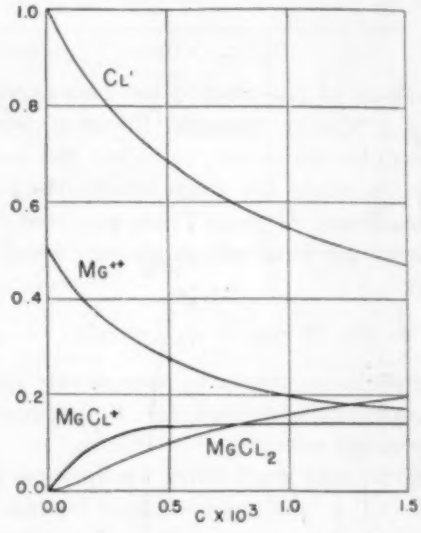

FIG. 2. Relative concentrations ($c\gamma_1$, etc.) of various species present in magnesium chloride-methanol solutions at 20°.

The Z-curve (solid circles) of Fig. 1 is a plot of (XXVII) for magnesium chloride in methanol at 20°. The parabolic loop of the Y curve for the same data has been pulled out to almost linear form by the new extrapolation function which, it will be recalled, is based on the hypothesis that the four species $MgCl_2$, $MgCl^+$, Cl' and Mg^{++} coexist over the range calculated. The tip of the parabola survives as an S in the curve near $Z = 3 \times 10^{-4}$, and a positive departure from linear approximation appears beyond $Z = 5 \times 10^{-4}$. Tinkering with the constants and recycling would, in our opinion, straighten the S; the flattening at high Z-values is probably due to the onset of higher association, such as $(MgCl_3)'$. It should also be borne in mind that only the leading term was used for activity

coefficients, and that mobility terms were approximated by D_{12} (in other words, a blanket 1-2 correction was made for a mixture of 1-1 and 1-2 electrolyte). Considering these approximations, and the assumptions that $K = k_1$ and $\lambda^0_1 = \lambda^0_3$, the approach of the $\Lambda' - Z$ curve to linearity is satisfactory. From it, we obtain $\Lambda_0 = 97.5$ and $k_2 = 5 \times 10^{-4}$.

The value of Λ_0 is probably reliable, because it is obtained as the result of a short extrapolation of a theoretically linear function, and we recall that the approximation errors in it reduce to zero as c approaches zero. But it must be emphasized that the k's are at best established only to order of magnitude: they contain all the errors of the approximations made in using only leading terms for long range effects and, furthermore, they are obtained from the slopes of linear approximations to curves.

Fig. 2 summarizes the various equilibria present. We calculated γ_1 to second approximation by returning $\Lambda_0 = 97.5$ to (24) and calculated γ_3 in second approximation from the equation

$$\gamma_3 = \gamma_1/(1 + 2k_2/cf_2\gamma_1) \qquad \text{(XXX)}$$

where we used $k_2 = 4.9 \times 10^{-4}$; (the result of the $\Lambda' - Z$ extrapolation). The resulting values were used to recompute k_1 explicitly by (VI): the values scattered between 3 and 5 x 10^{-4}, averaging to 4.0 x 10^{-4} as second approximation to k_1. Then using (V) and (VIII), the relative concentrations of Mg^{++} and $MgCl_2$ were computed. It will be noted that Cl' and Mg^{++} begin to disappear quite rapidly as concentration increases from zero, as might be expected with constants of the order of 10^{-4}. As suggested in the introduction, $MgCl^+$ is the first associated species to form; unlike the bolaform electrolytes, however, the neutral $MgCl_2$ cluster also appears in significant amounts, even at fairly low concentrations. Already at 10^{-3} normal, about half (55%) of the total chloride is electrostatically bound, and the free magnesium ion concentration has dropped to 40 per cent. With increasing concentration the relative concentrations of $MgCl_2$ and $MgCl^+$ continue to increase, the chloride ions vanishing first into $MgCl^+$ ions, and then these in turn going to neutral $MgCl_2$ clusters with more chloride ions. In Fig. 1, it was seen that marked deviations from approximate linearity set in at about $10^{-3}N$. It has been shown (18) that a critical concentration

$$c_0 = 3.2 \times 10^{-7} D^3 \qquad \text{(XXXI)}$$

exists for 1-1 electrolytes beyond which higher association than pairwise must be considered; for methanol, this is about $0.01N$. The numerical coefficient in (XXXI) contains the cube of the valence product (z_1z_2); for a 2-1 salt in methanol, therefore, we would theoretically expect equilibria of higher order than those described by k_1 and k_2 to begin to be significant at the order of one eighth of the 1-1 critical concentration, and indeed, this is precisely where our approximate treatment ceases to be satisfactory.

REFERENCES

1. T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.*, **56,** 1066 (1934).
2. R. M. Fuoss, *Chem. Revs.*, **17,** 27 (1935).
3. R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, **73,** 269 (1951).
4. R. M. Fuoss and V. F. H. Chu, *ibid.*, **73,** 949 (1951).
5. M. H. Elliott and R. M. Fuoss, *ibid.*, **61,** 249 (1939).
6. C. R. Witschonke and C. A. Kraus, *ibid.*, **69,** 2472 (1947).
7. M. M. Davis and E. A. McDonald, *J. Research Nat. Bur. Stand.*, **42,** 595 (1949).
8. L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36,** 2689 (1932).
9. L. R. Dawson and W. M. Keeley, *J. Am. Chem. Soc.*, **73,** 3783 (1951).
10. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York (1943); Eq. (3-4-4).
11. Ref. (10), Eq. (4-3-42a).
12. Ref. (8), p. 2778.
13. G. Åkerlöf, *J. Am. Chem. Soc.*, **54,** 4126 (1932).
14. International Critical Tables, *V*, p. 11, McGraw-Hill Book Co., Inc., New York (1933).
15. A. Unmack, E. Bullock, D. M. Murray-Rust, and H. Hartley, *Proc. Roy. Soc.* (*London*), **A132,** 427 (1931); J. E. Frazer and H. Hartley, *ibid.*, **109,** 351 (1925).
16. W. N. Maclay, Thesis, Yale University, 1950.
17. R. M. Fuoss, *J. Am. Chem. Soc.*, **57,** 488 (1935).
18. R. M. Fuoss, *ibid.*, **57,** 2604 (1935).

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Hydrogen Overvoltage on Bright Platinum[1]

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ABSTRACT

A technique was used which allowed the confirmation of surface cleanliness of bright platinum electrodes during overvoltage measurements.

As the current density was increased, three consecutive η vs. i relationships were observed,

$$\eta = a_1 + b_1 i \quad \text{(I)}$$

$$\eta = a_2 - (0.026 \pm .003) \log i \quad \text{(II)}$$

$$\eta = a_3 - (0.105 \pm .015) \log i. \quad \text{(III)}$$

The current density at which the transition from (II) to (III) occurred was dependent on the rate at which hydrogen ion diffused into the double layer. The mechanism of hydrogen overvoltage on platinum is discussed in view of these results. The true area of the platinum electrode was determined from double-layer capacity measurements.

INTRODUCTION

Several investigators (1–6) have shown the importance of surface activation or cleanliness and solution purity for electrochemical investigations on platinum electrodes.

The reversible hydrogen potential at a platinum electrode requires that both the forward and reverse reactions of the over-all process $2H^+ + 2e \rightleftharpoons H_2$ take place. Grahame (7) showed that when the reduction of an ion occurs reversibly at an electrode surface the differential capacity of the electrode is enormously increased. He called this effect the "pseudocapacity." A pseudocapacity would, therefore, be expected for a platinum electrode in the vicinity of the reversible hydrogen potential. Ershler, Proskurnin, and Dolin (5) have shown that such a pseudocapacity exists for a clean, smooth platinum electrode in purified acid solutions. They found, by low frequency bridge measurements, that high differential capacities were obtained in the potential range from 0.0 to 0.25 volt anodic to the reversible hydrogen potential. It is also expected that this pseudocapacity would be found on cathodic polarization. The present investigation has shown that such a pseudocapacity is present on cathodic polarization for an overvoltage range of at least −0.1 volt from the reversible hydrogen potential.

By using a current interrupter technique developed by Schuldiner and White (8) it was found that the time-potential trace of a clean platinum electrode showed no measurable polarization decay during a 3000 microsecond interruption (Fig. 1a). This is because of the pseudocapacity caused by the reversible hydrogen reduction at the platinum surface. It was also noted that when impurities, even in very minute amounts, were on the platinum surface there was a definite polarization decay during the same interruption interval which was displayed as a rounding off of the leading edge of the time-potential trace (Fig. 1b–1e). The initial rapid change in potential shown on these traces was caused by the *IR* drop from the reference electrode to the cathode interface. This potential change was used to correct the overvoltage measurements for the *IR* drop (8). These time-potential traces were therefore used during overvoltage measurements for the double purpose of confirming surface cleanliness and correcting the series resistance error.

The impurity plated out on the platinum cathode shown in Fig. 1e was removed by prepolarizing the solution overnight. This demonstrated the effectiveness of the technique used in the removal of trace impurities.

EXPERIMENTAL METHOD

The electrolytic cell construction (Fig. 2), solution purification, prepolarization, and hydrogen purification procedures generally followed the techniques and requirements designated by Bockris (9) for overvoltage work. The prepolarization cathode was a mercury pool connected to the main cell through a stopcock. During overvoltage measurements, the stopcock was closed and the mercury was cathodically protected by passing a very small current to it via the platinum wire electrode above it. This polarized the mercury to a potential of over −0.5 volt. Solution of the mercury or other material

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picked up during the prepolarization was thereby prevented. The high overvoltage of mercury made it a more efficient cathode for cleaning the solution by prepolarization.

The platinum cathode consisted of grade A platinum (99.99%) and was in the form of a small sphere at the end of a very short length of wire. The apparent area of the electrode used to obtain the data shown in this paper was 0.034 cm² although electrodes of several other sizes were used in this study. The platinum sphere was formed by melting the end of a piece of wire. The electrode was sealed off by a glass rod which was then suspended in the solution. The anode was a platinum wire separated from the solution in the main cell by a fine fritted glass disk. An opening was left at the top of the tube

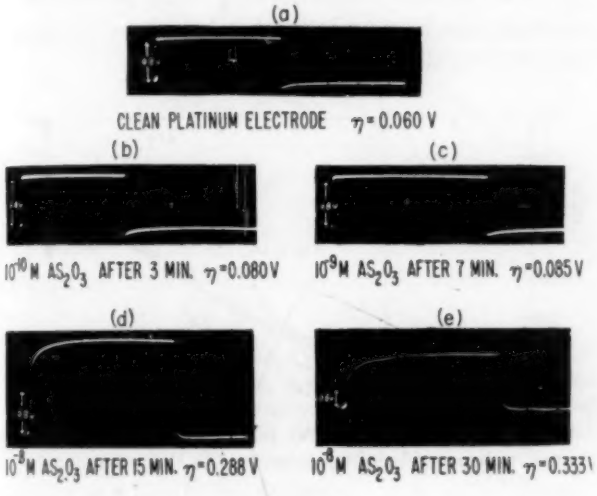
(a)
CLEAN PLATINUM ELECTRODE η = 0.060 V
(b)
(c)
10^{-10} M As_2O_3 AFTER 3 MIN. η = 0.080 V
10^{-9} M As_2O_3 AFTER 7 MIN. η = 0.085 V
(d)
(e)
10^{-8} M As_2O_3 AFTER 15 MIN. η = 0.288 V
10^{-8} M As_2O_3 AFTER 30 MIN. η = 0.333 V

FIG. 1. Effect of As_2O_3 on the time-potential trace of a platinum cathode. (0.1*N* H_2SO_4; current density; 0.0131 amp/cm²; 3000 microsecond interruption; area of electrode, .073 cm².)

holding this electrode to permit the escape of most of the oxygen formed at the anode. The platinum reference electrode was a wire mesh placed over an opening which led to the reference electrode in a side arm of the cell. The platinum reference electrode was used in the viewing circuit of the interrupter and the time-potential trace on the oscilloscope screen represented the potential change between the platinum cathode and this reference electrode during current interruption. The potential of the cathode was determined by means of a glass reference electrode placed in the side arm. This electrode was frequently calibrated against a hydrogen electrode in the same solution. The series resistance component of the overvoltage measurements, which consisted of the *IR* drop from the cathode interface to the point in the solution where the tip of the glass electrode entered the cell, was corrected for by use of the platinum reference electrode both of which were essentially in the same position in the electric field of the solution. The input impedances of both of these measuring circuits were very high so that no polarization of the reference electrodes would occur. The cathode potential was determined with a Beckman *p*H meter. The current interrupter and circuit connections used were the same as described by Schuldiner and White (8), with the exception that the maximum interrupter interval was increased to 3000 microseconds.

After the cell was charged with solution, the solution was boiled in an atmosphere of hydrogen for about an hour. The solution was then prepolarized at currents from 50 to 100 μa for a period of at least

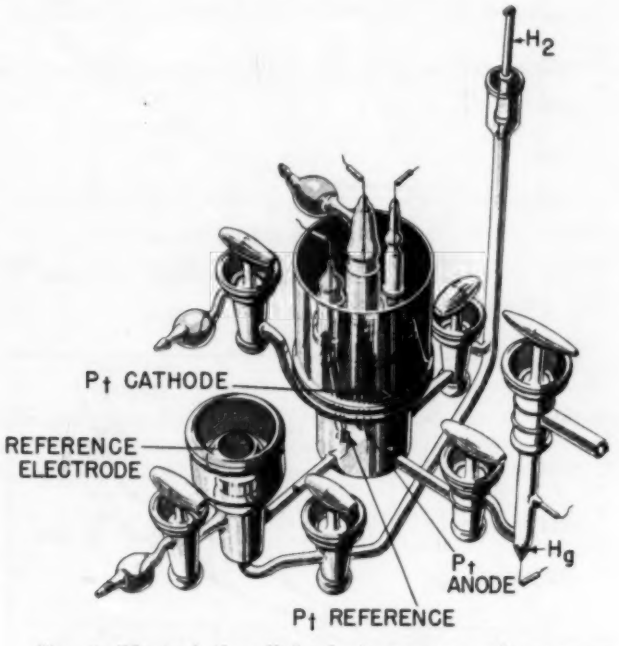

FIG. 2. Electrolytic cell for hydrogen overvoltage measurements.

24 hours during which it was continuously stirred by a stream of purified hydrogen. All openings to the cell were sealed by liquid to prevent oxygen or other atmospheric contaminants from entering. The cell temperature was maintained at 25 ± 1°C in a constant temperature room.

Before overvoltage measurements were made, the platinum cathode was cleaned by anodizing it for a period of one to five minutes using currents of about 25 to 50 μa. There was no measurable roughening of the surface by this treatment. This was verified by both prolonged anodizations and checking against the same electrode cleaned with hot nitric acid and heated white hot. Butler and Armstrong (2) also found that this anodic treatment was not deep-seated and that the oxidation of the platinum surface did not exceed one atomic layer. The amount of

oxygen formed as such or as an oxide of platinum did not exceed 2×10^{-7} g equivalents and this was largely removed before overvoltage measurements were made by opening the circuit and passing a stream of hydrogen over the cathode until the reversible hydrogen potential was steadily held. Low current measurements were practically always made by starting with a moderate current and successively decreasing it. This further decreased the probability of the effects of oxygen on the overvoltage at low currents. However, points were also determined by increasing the current density. These gave the same values. All overvoltage readings were taken in unstirred solutions, except where designated. In these cases the solution was stirred by a steady stream of hydrogen.

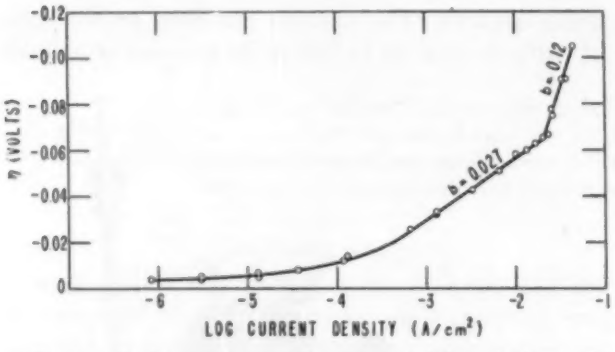

FIG. 3. Hydrogen overvoltage on bright platinum in 0.1*N* sulfuric acid solution.

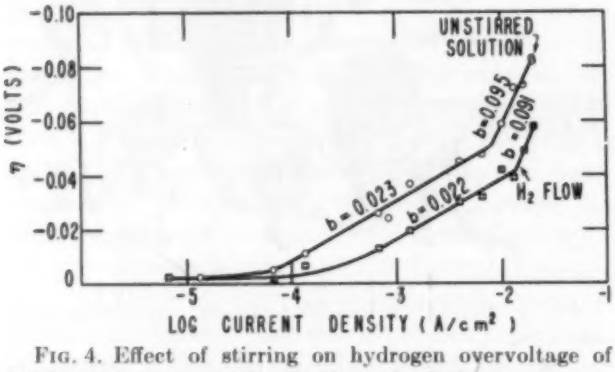

FIG. 4. Effect of stirring on hydrogen overvoltage of bright platinum in 0.05*N* sulfuric acid solution.

Overvoltage readings were taken within a few minutes after the polarizing current was applied. The cleanliness of the cathode surface was checked by means of its time-potential trace and the *IR* correction was made at the same time. Readings were steady as long as the time-potential trace indicated that no impurities were being picked up by the cathode. When this happened the potential readings became more negative. All potentials given are related to the reversible hydrogen electrode in the same solution.

Experimental Results

A typical platinum overvoltage curve for 0.1*N* sulfuric acid solution is shown in Fig. 3. The current density for this and all the following curves has been corrected for true surface area. The method used for making this correction is described in an appendix.

There are three distinct regions in this curve. The first, at the lowest current densities, represents a linear relationship between overvoltage and current density. It has also been observed by Hammett (10) and Dolin, Ershler, and Frumkin (11). This linearity can be attributed to the presence of a significant amount of the reverse process $H_2 \rightarrow 2H^+ + 2e$ in this current density range. Butler and Armstrong (2) treat the kinetics of the reversible hydrogen electrode for small currents and derive an expression showing this linear relationship between overvoltage and current density.

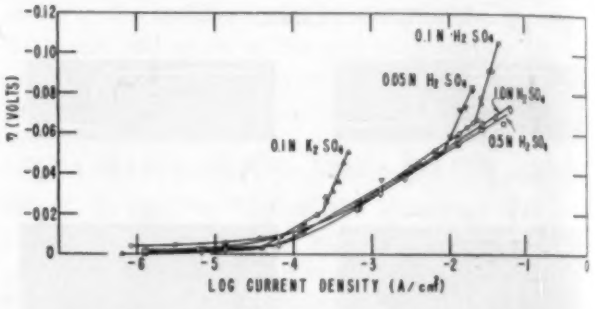

FIG. 5. Effect of *p*H and potassium ion on hydrogen overvoltage of bright platinum.

The second part of the overvoltage curve shows a Tafel relationship with $b = 0.026 \pm 0.003$. Replotting Hammett's (10) data for this region gives a value of $b = 0.027$ for bright activated platinum. Knorr (3) and Bockris (12) have also observed the same b value for this region.

The third region in the overvoltage-current density relationship shows a sharp transition in the rate determining mechanism with a resulting change in b to 0.105 ± 0.015.

Fig. 4 represents a typical experiment showing the effect of stirring the solution with a stream of hydrogen during overvoltage measurements. In this case the effect of concentration polarization is minimized which results in a displacement of the overvoltage curve to the right with no significant change in the shape of the curve.

*p*H *and Salt Effects*

The experimental results shown in Fig. 5 show the effects of *p*H and the introduction of potassium ion. It can be seen from these curves that there is only a

negligible, if any, pH or salt effect on the $b = 0.026$ section of the curve. However, these factors strongly influence the point of transition from the mechanism represented by the lower to higher b values.

If it is assumed that the pH effect is equal to $(RT/F) \ln a_{H^+}$ and the shift in overvoltage is calculated and compared with the experimentally determined value, the results shown in Table I are obtained. The salt effect was calculated using both the relation $(RT/F) \ln a_{K^+}$ and the expression derived by deBéthune (13) $- (RT/F) \ln [1 + (K^+)/(H_3O^+)]$. These results are also shown in Table I. A comparison of the experimental with calculated results shows a good agreement for both pH and salt effects. It should be mentioned that small changes in the b value will cause significant changes in the experimentally determined values of $\Delta\eta$, especially for the case where a large extrapolation is required. An improvement in the precision of determining b would be desirable. These results, however, certainly show that within the experimental error the measurements do fit the theoretically calculated results. These data also indicate a method for further work on the pH and salt effects.

(15), using this theory, show the evaluation of η for the catalytic mechanism as

$$\eta = (RT/\alpha F)\left[\ln 2e_0 \frac{kT}{h} - \frac{\Delta G_0^*}{RT}\right] + (RT/F)\ln \frac{a_H}{a_{H^+}} - (RT/\alpha F)\ln i, \quad \text{(IV)}$$

where, ΔG_0^* is the free energy of the formation of the activated complex in the combination reaction between two hydrogen atoms; e_0 is the standard electrode potential; a_H is the activity of the hydrogen atoms/cm² of electrode surface; a_{H^+} is the activity of hydrogen ions in the bulk of the solution; and α is equal to 2 until the surface is saturated with hydrogen atoms after which $\alpha \rightarrow 0$. The pH effect on overvoltage is expressed in the term $(RT/F) \ln (a_H/a_{H^+})$.

TABLE I. *Comparisons of experimental with calculated changes in overvoltage caused by hydrogen ion and potassium ion activities*

Solution	a_{H^+}	a_{K^+}	Experimental $\Delta\eta_{total}$	Calculated		
				$\Delta\eta_{pH}$	$\Delta\eta_{K^+}$	$\Delta\eta_{total}$
0.1N H_2SO_4	0.070[a]	0	0[d]	0[d]	0[d]	0[d]
0.05N H_2SO_4	0.037[a]	0	−0.017[d]	−0.016[d]	0	−0.016[d]
0.1N K_2SO_4	0.003[b]	0.050[c]	−0.134[d]	−0.081[d]	−0.067[d,f]	−0.148[d,f]
					−0.077[d,g]	−0.158[d,g]
0.1N K_2SO_4	0.003[b]	0.050[c]	−0.118[e]	−0.064[e]	−0.067[e,f]	−0.131[e,f]
					−0.077[e,g]	−0.141[e,g]

[a] Harned and Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).
[b] By pH determination. A mixture of K_2SO_4 + $KHSO_4$ is indicated. This was caused by the accumulation of hydrogen ions in the main compartment of the cell during pre-electrolysis with the remote mercury electrode.
[c] Lewis & Randall, "Thermodynamics," 1st ed., p. 362, McGraw-Hill Book Co., New York (1923).
[d] Using 0.1N H_2SO_4 as base.
[e] Using 0.05N H_2SO_4 as base.
[f] Assuming salt effect (13) $= -(RT/F)\ln[1 + (K^+)/(H_3O^+)]$.
[g] Assuming salt effect $= (RT/F)\ln a_{K^+}$.

Discussion

The results shown in Fig. 4 and 5 lead to interesting conclusions concerning the mechanisms of hydrogen overvoltage on platinum. Okamoto, Horiuti, and Hirota (14) in a statistical mechanical treatment of the catalytic mechanism of hydrogen overvoltage concluded that the catalytic mechanism would be rate determining until the metal surface was saturated with atomic hydrogen. At this point there would be a change in the rate determining mechanism to an electrochemical reaction. Kortüm and Bockris

If the atomic hydrogen saturation of the electrode surface caused a change in the rate determining mechanism as postulated by these authors, then a decrease in hydrogen ion activity should require a higher current density for the surface to become saturated with atomic hydrogen. This would be so because the experimental results show no significant pH effect in the $b = 0.026$ range which means that the ratio a_H/a_{H^+} is constant for all hydrogen ion activities. This leads to the conclusion that a_H must be decreased in the same proportion that a_{H^+} is decreased and, therefore, saturation of the surface should take place at higher current densities. The curves in Fig. 4 and 5 show conclusively that the opposite effect is taking place, that is, a decrease in hydrogen ion activity causes a change in rate determining mechanisms at a lower current density rather than a higher one.

The rate determining mechanisms postulated for

the hydrogen overvoltage on a platinum electrode are as follows. In the voltage range where b is 0.026 ± 0.003, the rate determining mechanism is most likely the catalytic reaction,

$$2(H_3O)^+ + 2e \rightleftharpoons 2H + 2H_2O$$

$$H + H \xrightarrow[\text{slow}]{} H_2 \cdot$$

The discharge mechanism itself is reversible while the combination of hydrogen atoms is rate controlling and determines the Tafel b value. However, as the current density is increased the hydrogen ion concentration in the double layer reaches a constant value at the point where the rate of diffusion of hydrogen ions from the bulk of the solution becomes slower than the combination reaction. At this point the rate of hydrogen ion diffusion would be rate controlling if it were not for a parallel hydrogen-producing reaction taking place at the electrode surface. This reaction is undoubtedly the direct reduction of water to atomic hydrogen. Such a mechanism has been postulated by Eyring, Glasstone, and Laidler (16) and it is also generally believed to hold for alkali solutions. Parsons (17) gives the following reaction for reduction of hydrogen from water molecules:

$$H_2O + e \rightarrow A^{\ddagger} \rightarrow H + OH^- \rightarrow \tfrac{1}{2}H_2 + OH^-,$$

where $A^{\ddagger}$ is the activated complex corresponding to the highest energy barrier over which the system passes during completion of the over-all reaction. The calculated b value for such a reaction is 0.118.

The over-all mechanism of hydrogen overvoltage on a platinum cathode would therefore be two parallel reactions:

(A) A catalytic controlled reaction

$$(H_3O)^+ \text{ solution} \rightarrow (H_3O)^+ \text{ double layer}$$

$$(H_3O)^+ \text{ d.l.} + e \rightleftharpoons H + H_2O$$

$$H \rightarrow \tfrac{1}{2}H_2$$

and

(B) a slow discharge controlled reaction

$$H_2O + e \rightarrow H + OH^-$$

$$H \rightarrow \tfrac{1}{2}H_2$$

both of which take place at all current densities. If we conclude that, virtual maximum rate[2] of discharge of protons from a water molecule < virtual maximum rate of combination of hydrogen atoms < virtual maximum rate of discharge of protons from hydronium ions, and also that at current densities below the transition point in b values, the net rate of diffusion of hydrogen ions from the bulk of the solution to the double layer is greater than the virtual maximum rate of the combination reaction; then in this range A is rate determining because this over-all reaction is faster than B. At current densities higher than the transition point the net rate of diffusion of hydrogen ions is slower than the virtual maximum rate of discharge of protons from a water molecule and here B is rate determining since its over-all reaction is now faster than A.

These conclusions are confirmed by the data shown in Fig. 4 and 5. The effect of stirring the solution would result in an increase in the rate of diffusion of hydrogen ions into the double layer and this would then require a higher current density for reaction B to be rate determining. The experimental results shown in Fig. 4 support this conclusion. The data shown in Fig. 5 also confirm these conclusions since they show that the hydrogen ion concentration does determine the current density at which the rate determining mechanism changes.

DeBéthune (13) in a study of the salt effect showed that from the Eyring, Glasstone, and Laidler theory (16) when the protons reduced at an electrode surface come from hydronium ions there will result an increase in overvoltage; and when the protons discharged come from water molecules, the overvoltage will be reduced. The results of this investigation show that the salt effect increases overvoltage in the $b = 0.105$ range. It was concluded in this paper that in this range the rate determining mechanism is the reduction of protons from water molecules and not from hydronium ions as would be required by deBéthune's postulate. However, these conclusions are not in complete contradiction as they may seem at first sight. This is because the point at which the change in mechanism takes place is determined by the hydrogen ion activity in the double layer in which range the catalytic reaction, A, is rate determining. In other words, the pH and salt effects which are only in the $b = 0.105$ range are determined in the range in which the catalytic reaction is rate determining and where the proton source is primarily from hydronium ions. The effect of the potas-

[2] This is a concept of Carl Wagner (private communication, April, 1952). He stated, "We may introduce the concept of the 'virtual maximum rate' of the various consecutive steps of a sequence $A_1 \rightarrow A_2 \rightarrow \cdots A_\gamma \rightarrow A_{\gamma+1} \cdots A_n$. The virtual maximum rate of an individual step $A_\gamma \rightarrow A_{\gamma+1}$ is defined as the rate which would be found if equilibrium for all the foregoing steps and all subsequent steps were established (e.g., with the aid of appropriate catalysts), i.e., the concentration of A_γ was determined by an equilibrium with the primary reactant A_1, and the concentration of $A_{\gamma+1}$ was determined by an equilibrium with the final reaction product A_n. Then we may say that the reaction with the lowest virtual maximum rate controls the overall rate."

sium ions is to decrease the concentration of hydrogen ions in the double layer.

Summary

1. A method of determining surface cleanliness of the platinum cathode was developed.

2. Platinum overvoltage curves in various concentrations of sulfuric acid and 0.1*N* potassium sulfate were determined.

3. Conclusions from the experimental results were used to postulate the mechanisms of hydrogen overvoltage on a platinum electrode.

Acknowledgments

The author is indebted to Dr. J. O'M. Bockris of Imperial College of Science and Technology and to Drs. J. C. White, H. W. Salzberg, and J. J. Lander of the Naval Research Laboratory for assistance both in the experimental work and in the theoretical discussions of this investigation.

APPENDIX

Determination of True Surface Area of the Platinum Electrode

It was found during overvoltage measurements in 0.1*N* potassium sulfate solution, that if the current was maintained at the highest current densities shown in Fig. 5 for this solution, a rapid and sudden increase in overvoltage would take place after about five minutes. The overvoltage data then obtained would result in a curve such as shown in Fig. 6. That the higher overvoltage curve was caused by some impurity being plated out on the platinum surface was evident in two ways. Initially, when the current was greatly lowered the voltage dropped considerably and the time-potential trace showed evidence of an impurity on the surface. Secondly, if the double layer capacity of the cathode surface was determined during the transition to the higher overvoltage curve and beyond, a double layer capacity vs. voltage curve such as shown in Fig. 7 resulted. This curve shows evidence of a pseudocapacity at about $\eta = -0.5$ volt. This is definite evidence that some trace material was eventually reduced at the cathode surface. The fact that after the pseudocapacity peak, the capacity comes to the same value as before the peak, shows that this impurity was not organic in nature.

The true surface area of the platinum electrode was determined from this double layer capacity data by assuming Grahame's value of 16 microfarad/cm² (7) for the capacity at the bottom of the curve. The data shown in Fig. 7 was corrected for this which resulted in an area correction of 2.16 times the apparent area of the platinum cathode. This correction for the area was used in all the data given in this paper.

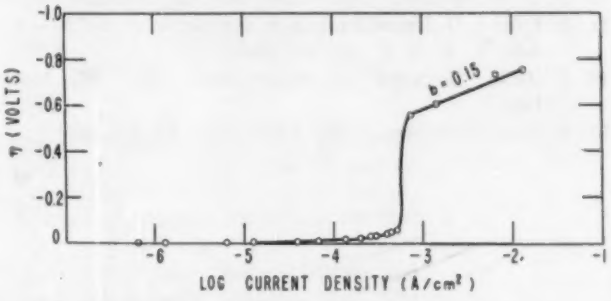

Fig. 6. Effect of residual trace of impurity on hydrogen overvoltage of bright platinum in 0.1*N* potassium sulfate solution.

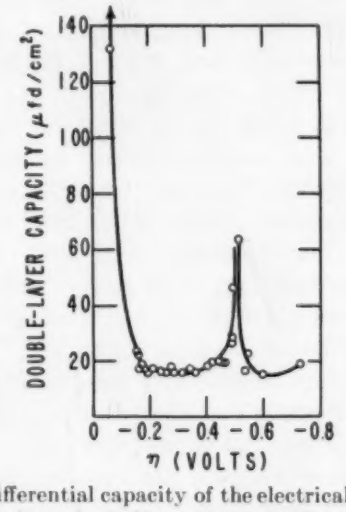

Fig. 7. Differential capacity of the electrical double layer on bright platinum in 0.1*N* potassium sulfate solution containing a residual trace of impurity.

The hysteresis effect on smooth platinum noted by Azzam and Bockris (18) can also be explained on the basis of these results.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the Journal.

REFERENCES

1. A. H. W. Aten and M. Zieren, *Trans. Am. Electrochem. Soc.*, **58**, 153 (1930).
2. J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, **1934**, 743.
3. C. A. Knorr, *Z. Elektrochem.*, **42**, 669 (1936).
4. A. Slygin and B. Ershler, *Acta Physicochim. U. R. S. S.*, **11**, 45 (1939).
5. B. Ershler and M. Proskurnin, *Acta Physicochim. U. R. S. S.*, **6**, 195 (1937).
   P. Dolin and B. Ershler, *Acta Physicochim. U. R. S. S.*, **13**, 747 (1940).
6. J. O'M. Bockris and B. E. Conway, *Trans. Faraday Soc.*, **45**, 989 (1949).

7. D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).
8. S. Schuldiner and R. E. White, *J. Electrochem. Soc.*, **97**, 433 (1950).
9. J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).
10. L. P. Hammett, *J. Am. Chem. Soc.*, **46**, 7 (1924).
11. P. Dolin, B. Ershler, and A. Frumkin, *Acta Physicochim. U. R. S. S.*, **13**, 779 (1940).
12. J. O'M. Bockris, *J. Electrochem. Soc.*, **98**, 153C (1951).
13. A. J. deBéthune, *J. Am. Chem. Soc.*, **71**, 558 (1949).
14. G. Okamoto, J. Horiuti, and K. Hirota, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 223 (1936).
15. G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, p. 432, Elsevier Publishing Co., Amsterdam, The Netherlands (1951).
16. H. Eyring, S. Glasstone, and K. J. Laidler, *J. Chem. Phys.*, **7**, 1053 (1939).
17. R. Parsons, *Trans. Faraday Soc.*, **47**, 1332 (1951).
18. A. M. Azzam and J. O'M. Bockris, *Nature*, **165**, 403 (1950).

Effect of Stress on Metal Electrode Potentials[1]

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ABSTRACT

The effect of stress on the electrode potentials of silver and gold has been measured. Tension renders these metals cathodic in aqueous solutions of their corresponding salts. Compression produces changes in the opposite direction. These changes are proportional to the applied load. Quinhydrone and ferrous-ferric electrodes are not affected by stress.

The observations cannot be accounted for on the basis of thermodynamic changes produced within the metal. Necessarily, a surface phenomenon is responsible. The condition of the metallic surface is shown to be an important variable, although studies of certain variables within the electrolyte have failed to reveal the nature of polarization.

INTRODUCTION

The present study was undertaken in an attempt to obtain fundamental information relevant to stress corrosion phenomena and to the problems of preparing reproducible and stable metal electrodes for laboratory use. With many metals, for example iron and nickel, it is almost impossible to prepare electrodes which exhibit the true thermodynamically reversible potential. Reasons for this difficulty are considered to be primarily of two types: (*a*) hardness, which may be the cause of large strains within the metallic lattice, and (*b*) surface polarization. If the effects of hardness were known, some light might be shed on the related problems of stress corrosion.

To simplify the situation as much as possible, the present experiments were primarily concerned with applied stresses within the elastic limit. Most metal specimens were cold-worked, for, as will be seen, annealed metals undergo permanent deformation at such low stresses that no significant potential data can be obtained. Nevertheless, some reproducible results have been obtained for increments of total stress above that present in the initial cold-worked specimens.

Many have measured electrode potentials of cold-worked vs. annealed metals, but often the results have been inconclusive. The iron electrode has been studied by Richards and Behr (1) and by Walker and Dill (2). Iron was reported to become cathodic when subjected to tensile stress within the elastic limit. The effects were temporary, although reproducible. However, Endo and Kanazawa (3) state that tensile stress produces an *anodic* change. Evans and Simnad (4) observe that iron becomes anodic with tension, but cathodic with compression. Giulotto (5) measured the potential of iron wire in aqueous ferrous sulfate solution as a function of tensile stress. He observed stable, reversible changes in the cathodic direction which were proportional to the applied stress (80 μv/10,000 lb/in.^{2}).

Some softer metals have also been studied, but again, the data are not always in agreement. Spring (6) in an early paper reported potential measurements of cold-worked vs. annealed specimens of the same metal in aqueous solutions of the corresponding metal salt. Tin, lead, cadmium, and silver became anodic with cold work, but bismuth became cathodic. Tammann and Wilson (7) performed similar experiments with copper, silver, zinc, lead, and cadmium. In 52 cases out of 67, the cold-worked electrode was anodic.

More recently, Nikitin and co-workers (8) have studied in detail the effect of tensile stress on the galvanic potential of several metals and alloys over a wide range of stresses up to rupture. A zinc alloy (Zn, Cu, Al), brass, iron, and copper became anodic with stress in aqueous solutions of zinc, cupric, ferrous and cupric sulfates respectively. Silver behaved in the reverse manner in silver nitrate solution. However, Gautam and Jha (9) working with copper, obtained results which contradict those mentioned above; they found that it becomes cathodic when subjected to tensile stress in aqueous cupric sulfate.

The changes reported in these papers are of the order of 0.01 to 0.5 mv/1000lb/in.^{2} (psi) for applied stresses which often covered the entire range up to rupture. In many of these experiments, no attempt was made to demonstrate stability and reversibility. For this reason, the data are considered of qualitative significance only. In the present work, an attempt

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has been made to overcome the above objections. Some interesting correlations have been made, although a complete explanation of the phenomena is not yet possible.

Experimental

Tension

Apparatus.—The arrangement is shown in Fig. 1. A simple beam balance, 1, was used to apply tension to the wire electrode held in chucks, e, e'. Tension was applied by adding weights to b or with the chainomatic device, 3. The chain was 22 in. in length with 16 1-in. lead balls suspended at equal intervals. This device was calibrated in terms of number of turns of the screw required to level the balance beam with unit weight on ballast pan, a.

A Leeds and Northrup type K-2 potentiometer in conjunction with a lamp and scale galvanometer of 0.00048 μamp/mm sensitivity (at one meter) was used for potential measurements. A saturated Weston cell was used as a standard.

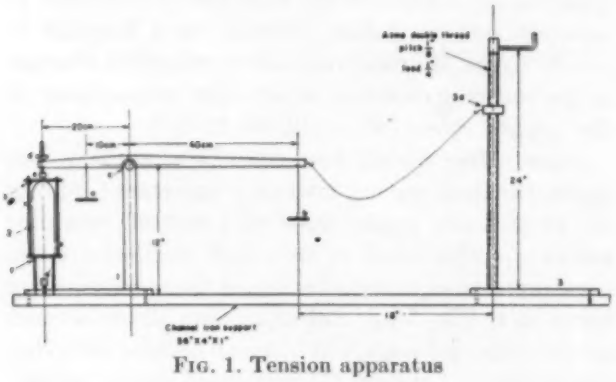

Fig. 1. Tension apparatus

Method.—Two freshly cleaned and straightened wires were sealed in the bottom holes of the glass cell (Fig. 2) with DeKhotinsky cement. Great care was exercised to keep the wire in the correct vertical position while the cement hardened.

The cell was placed in position on the brass tripod, the wire to be stretched was clamped in the chucks, and the adjustable legs on the tripod were raised so that the cell just made a snug fit with a rubber cushion on the tripod. With the beam exactly balanced by a ballast weight on a, turnbuckle d was adjusted until the balance beam just showed a deflection (as indicated by a small spirit level).

Aqueous electrolyte was added to the cell, the wires connected to the potentiometer circuit, and thermostatted water circulated through the cell jacket with a small rotary pump. This water was kept at 25.0 ± 0.1°C unless otherwise noted.

Potentials of this cell were found to vary considerably for periods ranging from an hour to one or two days. This variation often amounted to several millivolts. It was found that bubbling an inert gas (nitrogen) through the electrolyte for a few minutes at the beginning of the experiment shortened the period of erratic behavior. The requirement was obeyed that potentials must be stable to a few hundredths of a millivolt for at least 15 minutes before tension was applied.

In all experiments, the reference electrode was of the same metal as the test specimen, whenever possible taken from the same stock. Hence the initial potential of the resulting cell should have been zero at no applied stress. However, this ideal situation was rarely achieved. Often the starting potential

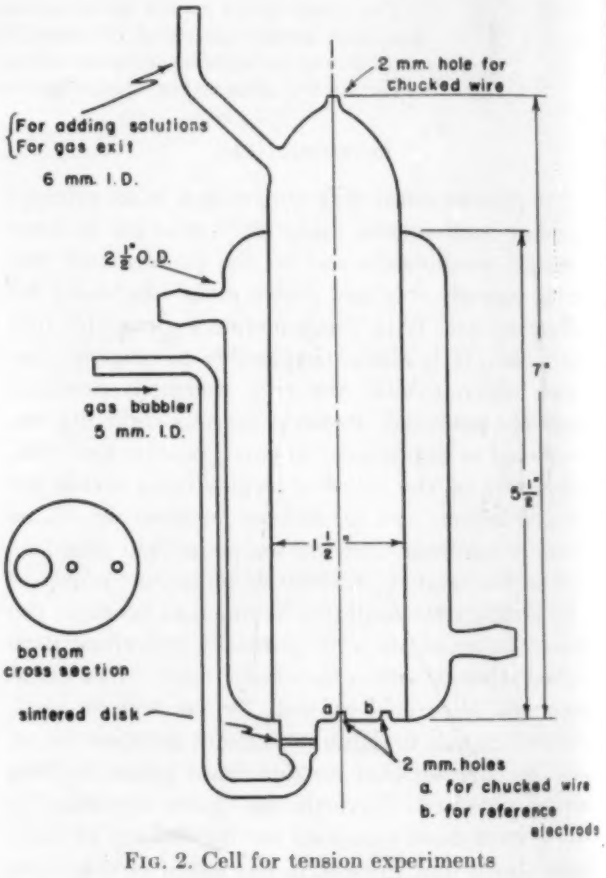

Fig. 2. Cell for tension experiments

amounted to several millivolts, and in a few cases was as high as 15 mv.

The following convention regarding signs was adopted: if the test wire was anodic to the reference electrode, the emf was designated negative.

After sufficient data were obtained by use of a given electrolyte, it was convenient to siphon off the solution through the sintered disk, and to add a new electrolyte without disturbing the cell. Whenever this was done, the cell was first thoroughly rinsed with the new solution.

Compression

Apparatus.—A small Carver hydraulic press was used to apply compressional stresses to coin shaped

metal specimens. The assembly is shown in Fig. 3. Electrolyte was contained in a Lucite beaker, 5, which had a 1-in. diameter hole in the bottom.

Method.—The Bakelite disk, 6b, was held in place with Duco cement. The upper disk, 6a, and the steel plunger, 4, contained holes as indicated for the wire connecting the specimen, 7, with the potentiometer circuit. This wire was of the same metal as the test specimen in all cases. The specimen contained an oversize hole along its cylindrical axis. The wire was inserted in this hole and a tight connection made by crimping the surrounding metal. Insulation from the plunger was achieved by the use of woven glass spaghetti tubing.

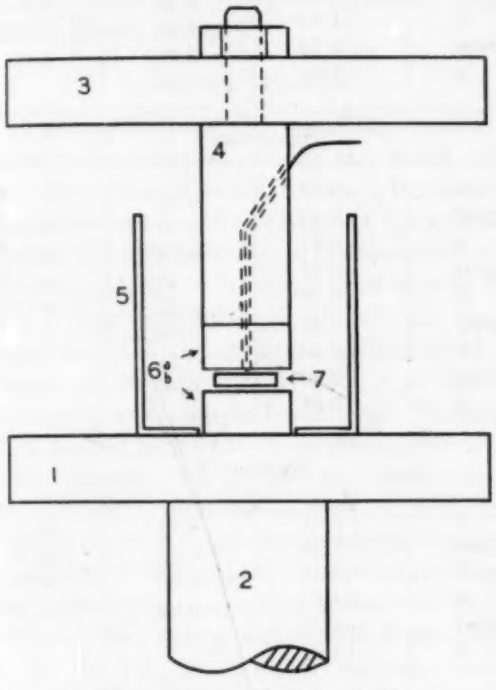

FIG. 3. Compression apparatus

The specimens were carefully machined to have faces parallel to a tolerance of less than one thousandth of an inch. These faces were subsequently polished lightly with fine metallographic paper. The cylindrical surfaces which were exposed to the electrolyte were prepared by a variety of means which will be described separately for each experiment.

After the apparatus was assembled as shown in Fig. 3, the hydraulic piston, 2, was raised until the gauge just showed a positive pressure. Then the fluid pressure was momentarily released. This was taken as the starting point for the application of known compressional stresses.

A reference electrode was suspended near the wall of the beaker. This was always of the same metal as the test specimen, and consisted of a short length of 0.025-in. wire, cleaned in dilute acid and/or lightly abraded.

The aqueous electrolyte was then added and cell potentials measured as described for the tension experiments. In some cases, a fritted bubbler was inserted in the solution, through which nitrogen was passed for purposes of mixing and removing temperature gradients, but this made no apparent difference in the results. The same criteria were used for satisfactory stability of potentials as described for the experiments with tensile stress. Stress applied to the specimen was calculated from the reading on the hydraulic gauge, and the known diameters of the piston and the specimen.

The Lucite beaker was not thermostatted for these experiments. However, the temperature of the room was always within the range 22–27°C and was constant to less than half a degree during each series of measurements. It is felt that this additional variable in the experiment is unimportant, since it was found that similar results were obtained whether or not the electrolyte was agitated by bubbling gas. That is, small thermal gradients are not of primary importance.

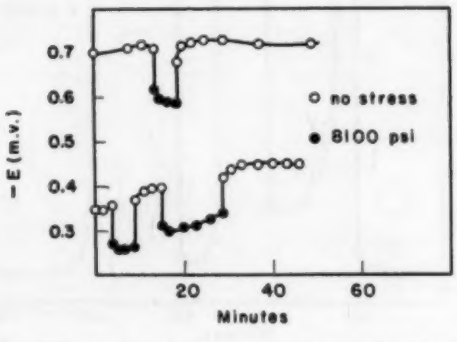

FIG. 4. Effect of tension on electrode potential of gold. (Electrolyte: 0.06*M* $HAuCl_4$).

RESULTS

The experiments are classified in four groups:

1. Experiments with electrodes in contact with an aqueous solution of the corresponding metal salt.
2. Experiments with silver to test the importance of chemical variables.
3. Experiments to test the importance of condition of the metal surface.
4. Experiments in which the metal served as an indicator electrode with no common ion in solution.

Tension and Compression Experiments

Gold.—The tension experiment utilized 0.025-in. cold drawn wire, 99.9 per cent pure. The surface was cleaned with acetone, followed by concentrated hydrochloric acid. Aqueous 0.06*M* $HAuCl_4$ was the electrolyte. Typical results are shown in Fig. 4. Tensile stress invariably made the wire more noble. The effect is essentially stable and reversible.

The compression experiment utilized a cylinder of fine gold, 0.51-in. in diameter and 0.64-in. long. The surface was carefully machined, then cleaned in carbon tetrachloride just before use. The electrolyte was the same solution used in the previous experiment. Results are shown in Fig. 5. Compression produced a stable, reversible potential change in the anodic direction, opposite to that produced by tension.

Silver.—The tension experiments utilized 0.025-in. wire which had been cold drawn from 99.98 per cent pure metal melted in vacuo. Surfaces were abraded lightly with 2/0 metallographic paper, then cleaned in acetone, 1:10 nitric acid, and distilled water. The electrolyte was 0.1*M* silver nitrate. Typical results are shown in Fig. 6 and given in Table I. Potential

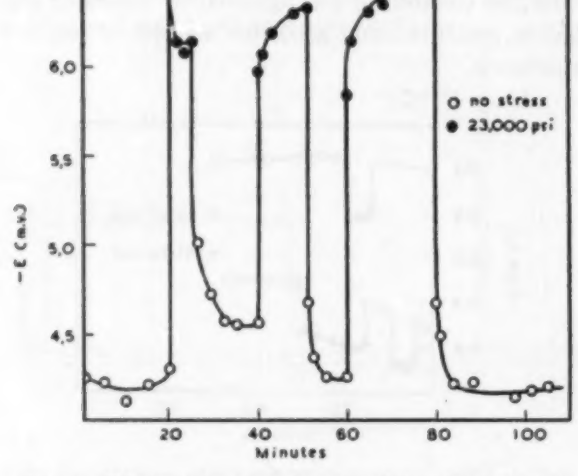

FIG. 5. Effect of compression on electrode potential of gold. (Electrolyte: 0.06 *M* $HAuCl_4$).

changes produced by tension were always in the cathodic direction and proportional to the applied stress.

Stresses applied suddenly (by adding a weight to pan *b*, Fig. 1) or gradually (by using the chainomatic device) apparently produced the same effect. Hence, the two methods were used interchangeably in later work. At higher stresses (16,000 psi), potential changes were less stable and not entirely reversible. This may be associated with the onset of appreciable amounts of plastic deformation. For a single experiment, a wire was used which had been annealed in vacuo for 16 hours at 450°C. The relatively small applied stress of 1800 psi stretched the wire beyond the elastic limit, which resulted in an abnormally large (cathodic) but irreversible change in potential.

From a large number of experiments with hard drawn wire from two different sources, the "tension coefficient" for the silver electrode potential was

TABLE 1. *Effect of tension on electrode potential of silver* (Electrolyte: 0.1*M* $AgNO_3$)

Stress (psi)	Average *E* (mv)	$\lvert \Delta E \rvert$	$\lvert \Delta E \rvert$/1000 psi
Specimen 1			
0	1.66		
		0.12	0.057
2120	1.78		
		0.14	0.066
4240	1.92		
		0.33	0.078
0	1.59		
		0.43	0.081
5300	2.02		
		0.42	0.079
0	1.60		
		0.16	0.076
2120	1.76		
		0.50	0.094
7420	2.26		
		0.41	0.078
2120	1.85		
		0.14	0.066
0	1.71		
		0.41	0.077
5300	2.12		
		0.40	0.076
0	1.72		
		1.03	0.097
10600	2.75		
		0.79	0.075
0	1.96		
Specimen 2			
0	−0.19		
		0.32	0.101
3180	0.13		
		0.30	0.094
0	−0.17		
		0.74	0.140
5300	0.57		
		0.53	0.100
0	0.04		
		0.23	0.072
3180	0.27		
		0.33	0.104
0	−0.06		
		0.51	0.096
5300	0.45		
		0.44	0.082
0	0.01		
Specimen 3			
0	−6.17		
		0.74	0.140
5300	−5.43		
		0.31	0.146
7420	−5.12		
		0.82	0.110
0	−5.94		
		0.36	0.113
3180	−5.58		
		0.33	0.104
0	−5.91		

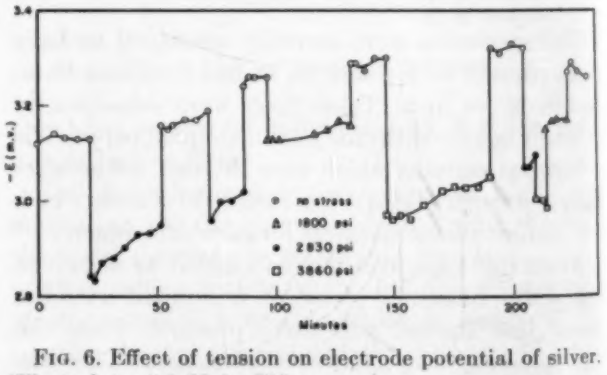

FIG. 6. Effect of tension on electrode potential of silver. (Electrolyte: 0.1 *M* $AgNO_3$).

found to be 0.078 ± 0.021 mv/1000 psi up to total stresses of 10,000 psi. However, with some specimens, the coefficient was as low as 0.01. This matter is considered further in the experiments dealing with various methods of surface preparation. It is clear

that these data are not quantitatively indicative of some property of silver, and yet a proportionality between potential change and applied stress exists for any given specimen.

The compression experiments were performed with 1/8-in. disks cut from 5/8-in. diameter rod of the same purity metal used in the tensile tests but of unknown metallurgical history. The rod had been swaged and was quite hard; compressional stresses of 30,000 psi produced no appreciable plastic deformation. Surfaces were cleaned as described for silver wires. The silver disks became anodic with compressional stress. Again, the changes were stable, reversible, and proportional to the applied stress but opposite in direction to the effects produced by tension. Typical results are shown in Fig. 7.

Solution Variables

It is apparent from the preceding results that thermodynamic changes within the metal cannot explain the effects of stress, for work input (stress) must always raise the free energy of the metal and change its electrode potential in the anodic direction. Furthermore, simple calculations show that for silver with a Young's modulus of 10^7 psi, the thermodynamic potential change upon application of 1000 psi stress will be only 0.04 μv even if all the work introduced is available as free energy. Thus, some type of surface phenomenon is responsible for the observed changes. The following experiments were designed to test several variables which might give a clue to the cause of the electrode polarization.

Dependence on silver nitrate concentration.—Typical tension experiments were performed with 0.025-in. silver wire with a series of electrolytes which varied from 10^{-4} to 1M. In all cases, cathodic potential changes were observed, similar to those shown in Fig. 6. The proportionality between ΔE and stress varied somewhat from one experiment to another, but there did not appear to be any correlation with the electrolyte concentration.

Effect of tension in the absence of silver ion.—The following electrolytes were utilized in this experiment: 0.1M NH_4NO_3, 0.1M Na_2SO_4, 0.1M KI. With all of these, tension produced potential changes in the cathodic direction. However, comparatively large stresses (6000–8000 psi) were required to produce potential changes of 0.1–0.2 mv. Furthermore, the change was manifested slowly over a period of several minutes. The reciprocal effect obtained on removal of the stress. That these phenomena are real was proved by determining the tension coefficient in a silver nitrate solution before and after each experiment with these other electrolytes. Invariably, the typical instantaneous, relatively large and permanent potential changes were observed. It should be mentioned that with silver nitrate solutions, the entire potential change usually occurred within ten seconds after stress was applied, which was the minimum time required to balance the potentiometer.

Dependence on pH.—Several tension experiments were performed in 0.1M silver nitrate containing varying concentrations of ammonium hydroxide from from 0.3 to 16.4M. For the 16.4M solution, dry ammonia was bubbled through the solution during the entire experiment. In all cases, the effect of tension (2830 psi) was to render the test specimen cathodic. The tension coefficient decreased somewhat with increasing pH, but this is not considered significant, since the wire was being etched at a slow rate (see Discussion).

Dependence on dissolved gases.—Tension experiments were performed in which argon, nitrogen, and carbon dioxide were separately bubbled through the

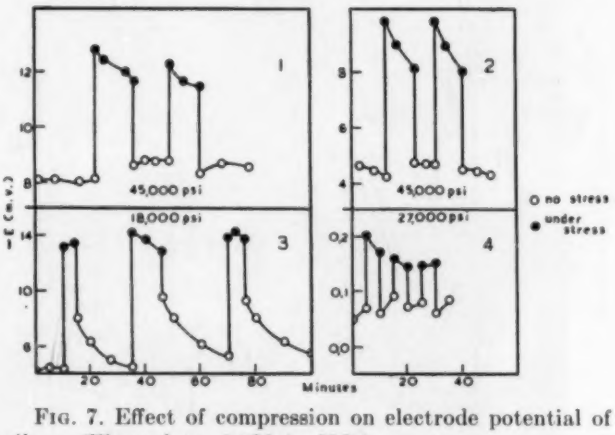

FIG. 7. Effect of compression on electrode potential of silver. (Electrolyte: 0.1M $AgNO_3$).

0.1M silver nitrate solution. The gases were freed of oxygen by passage over copper at 245°C. Cell potentials were measured in each case while the gas was bubbling. For the test with argon, the gas was allowed to bubble for 30 hours before stress was applied. Within the normal variation of results, the tension coefficient was independent of the nature of the gas.

To determine if extremely small amounts of oxygen are responsible and sufficient for the observed effects of stress, a careful tension experiment was performed which utilized water freed of oxygen according to the method of Patrick and Wagner (10). The method involves refluxing the water with Wood's metal. Water so purified in an argon atmosphere was distilled directly into a flask which contained sufficient silver nitrate crystals to render the resulting solution 0.1M. This solution could be forced into the cell shown in Fig. 8 with argon pressure without exposure to the atmosphere.

The chucks were machined from pure silver rod; the external clamps were of aluminum. Rubber

sleeves connected the rods to the glass cell. The reference electrode consisted of a cylinder of 0.010-in. pure silver sheet, 2 in. high and diameter as large as the cell. A silver wire was spot welded to it and brought out through a. The test specimen was 0.040-in. diameter wire prepared from 99.98 per cent silver. It was melted in vacuo and swaged and drawn to the final size from a $\frac{5}{16}$-in. casting without intermediate annealing.

After assembly, all possible leaks were sealed with DeKhotinsky cement. The specimen was cleaned anodically in a solution which contained 60 grams each of potassium ferrocyanide and sodium cyanide per liter. A total time of five minutes and current density of 10–15 amp/dm^2 were the conditions used. After the experiment, it was noted that the surface was truly electropolished only in spots, although the entire surface was stripped of oxides which may have

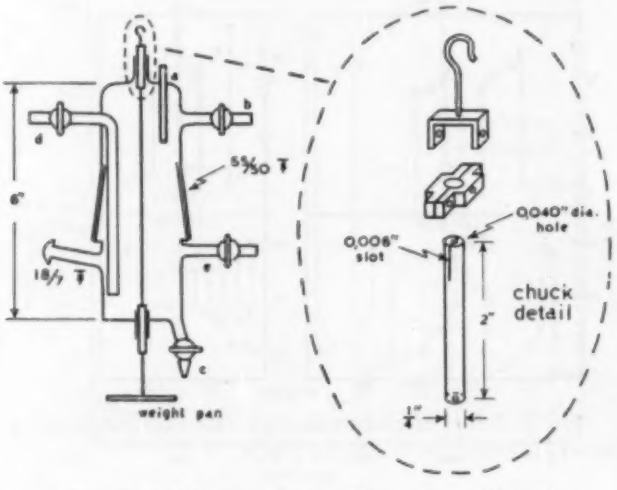

FIG. 8. Cell for oxygen-free tension experiment

been present. After the cyanide solution was drained off through c, the cell was rinsed four times with purified water from an additional reservoir in the purification system. Finally, the silver nitrate electrolyte was transferred to the cell and mixed thoroughly by the argon bubbler d. Measurements were made with argon passing over the surface of the solution at e.

At the conclusion of the experiment, the electrolyte was tested for dissolved oxygen by the Winkler reaction (11). The silver oxide formed is easily converted to the iodide when the solution is acidified and the starch-iodine endpoint is clear though somewhat slow. This test was completely negative in the solution used, which allows the estimation of an oxygen content of $\leq$0.05 cc per liter.

Results were obtained on three consecutive days and were similar to previous data obtained. It is clear that tension renders silver cathodic even in a solution in which the dissolved oxygen content is $\leq$0.05 cc per liter.

Tension coefficient in presence of a wetting agent.— A typical tension experiment was performed in 0.1*M* silver nitrate to demonstrate that the system was behaving in the expected manner. A tension coefficient of 0.04 mv/1000 psi was observed. To this solution was added 7 mg of Duponol ME Dry detergent. Nitrogen was passed through for a few minutes to ensure adequate mixing. Much frothing occurred, but it was possible to measure the effect of tension. A typically stable and reversible potential change in the cathodic direction of 0.04 mv/1000 psi was observed.

Condition of Electrode Surface

Some early experiments indicated that silver wires which had been chemically etched with ammonia or cyanide failed to exhibit a change in potential with applied stress. These observations raised questions concerning the importance of surface geometry and surface strains.

A series of compression experiments was run in 0.1*M* silver nitrate with the usual coin-shaped silver specimens but with the surfaces prepared in various ways.

1. Surface stroked lightly with 2/0 metallographic paper in the direction of the circumference.
2. Surface machined on lathe with automatic drive, with very fine cut.
3. Surface electropolished in the same cyanide solution described earlier; current density 15–20 amp/dm^2 for five minutes.

All were cleaned in ethyl alcohol and carbon tetrachloride and allowed to dry in air at room temperature just before use.

4. Surface abraded with 2/0 metallographic paper and cleaned in 1*M* perchloric acid for 30 minutes.

After the system was assembled, iron accidentally came into contact with the electrolyte and produced some galvanic action. The deposited silver formed a rather adherent coat on both the disk and reference electrode. Nevertheless, a compression experiment was performed with this specimen.

Results are shown in Fig. 7. The effects are not as stable as some considered earlier, perhaps due to the high applied stresses which probably produced some plastic deformation. Yet, it is clear that specimen 4 shows only a small compression coefficient, 1, 2 show a larger effect, and 3 the largest.

To determine if this is, in fact, a function of surface roughness, specimens 2, 3, and 4 were sacrificed as follows to photograph a cross section. The specimens were electroplated with copper to protect the surface during the cutting process. The cut was made along the diameter with a jeweler's saw, and the slice mounted in plastic in the usual manner. After the surface was polished, a photomicrograph was taken which showed the copper-silver interphase. This is

the contour of the cross section of the original silver surface. Photomicrographs of these specimens are shown in Fig. 9. The light area is silver, the gray, copper. For specimen 4, the silver surface was so rough and loose that the copper plate did not adhere properly. Thus, due to the poor protection, some silver may have been lost in the cutting and mounting processes and hence, the photomicrograph shows only a minimum roughness of the original surface.

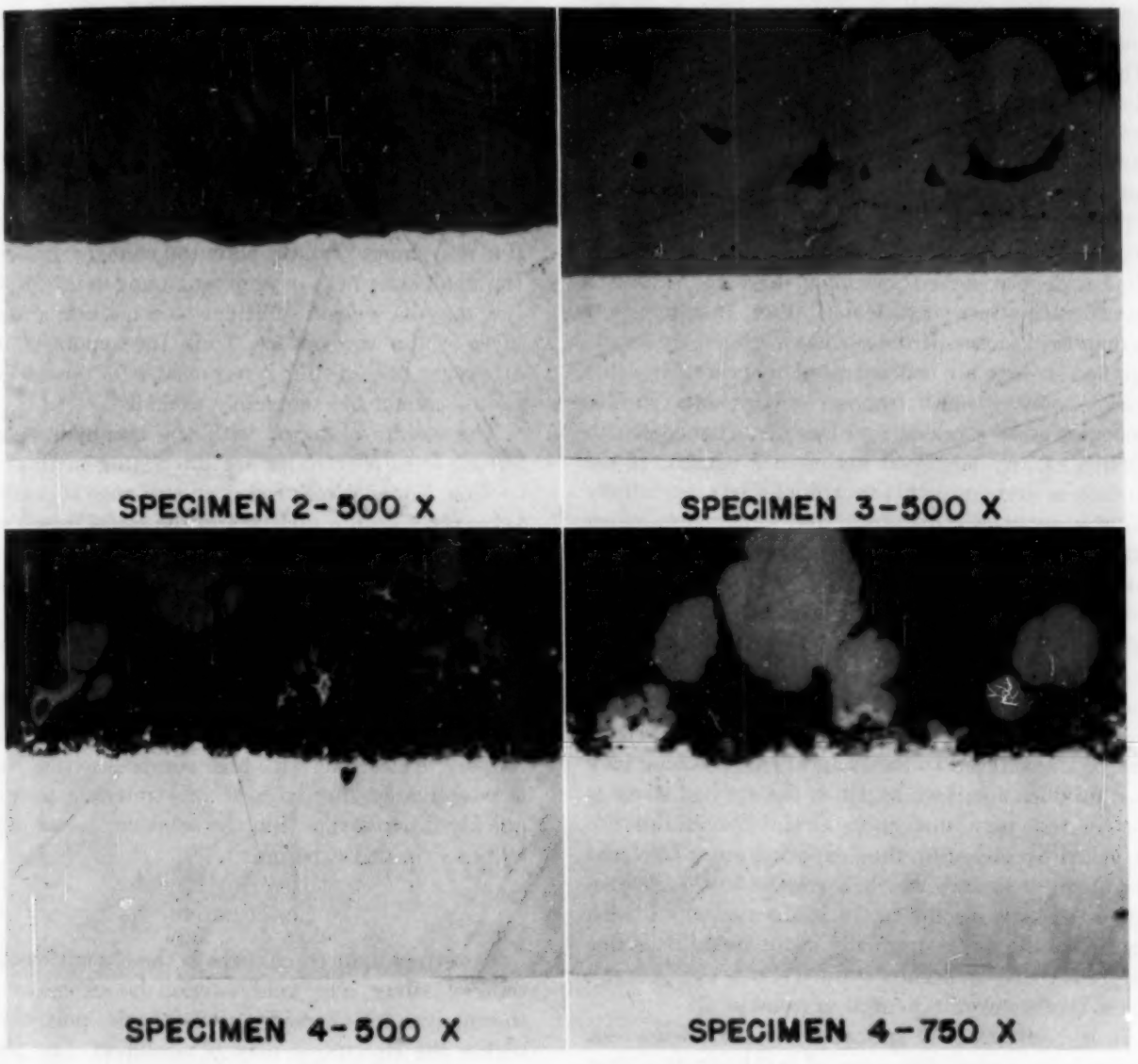

FIG. 9. Photomicrographs of silver surfaces

Indicator Electrodes

Two tension experiments with a different type of cell were performed.

1. Electrodes of 0.025 in. platinum wire in a Clark and Lubs buffer of pH = 4 saturated with quinhydrone. The wires were cleaned in concentrated hydrochloric acid and distilled water before use. No detectable potential change was observed upon application of 9000 psi stress.

2. A similar experiment was performed with gold wires and an electrolyte 0.1M each in ferrous chloride, ferric chloride, and hydrochloric acid. The experiment was carried out immediately after the corresponding one with $HAuCl_4$ electrolyte. Potentials were stable to 0.01 mv, but no change could be detected on application of 8100 psi stress.

The latter experiment was repeated with compressional stress, again immediately after the corresponding one with $HAuCl_4$ electrolyte. The same ferrous-ferric electrolyte was used. A small transient change in potential of 0.1 mv (cathodic) was observed when 34,000 psi stress was applied. Removal of the stress produced a transient change in the reverse direction. This cycle was repeated several times. The temporary nature of the changes is con-

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sidered significant, since the experiment performed immediately before with $HAuCl_4$ electrolyte showed the usual stable and larger changes.

Discussion

It has been shown that the observed changes in electrode potential upon application of stress are too large to be accounted for on thermodynamic grounds and are often in the wrong direction. It seems clear that some form of surface phenomenon is responsible. That the nature of the surface is a factor has been demonstrated. An electropolished metal, presumably relieved of surface strain gradients, shows a larger stress coefficient of potential than a metal with a relatively rough surface which has been cold worked. This indicates that strain gradients are not necessary for the phenomenon to appear in spite of the fact that a deeply etched specimen does not exhibit a measurable stress coefficient. Rather, this may be a geometrical factor. If the surface is extremely rough, applied stresses are concentrated in corners. In other words, only a small fraction of the total surface becomes more strained and less disturbance or distortion of any adsorbed material is caused. If the surface is very smooth (electropolished), essentially all of it acquires some strain and a maximum effect of stress on the potential is produced. A surface which has received a coating of electrodeposited metal shows only a small change in potential with applied stress. This is consistent with the present argument since the fresh surface is not only geometrically rough, but not an integral part of the substrate metal. Thus only part of the applied stress can be transmitted to the surface. Deep etching may also produce a surface in which the applied stress is distributed very unevenly. Grain boundaries are attacked by etchants, thus exposing more area and producing a surface which is similar to the electrodeposited one insofar as it is discontinuous with respect to the strain originally in the metal. It is not surprising that an etched surface shows only a small stress coefficient of potential or none at all.

It is interesting to speculate on the mechanism of the polarization. One type of polarization is that which involves mobile ionic species within the electrolyte (concentration polarization). For example, if ions absorbed on the metal surface are ejected into the solution when stress is applied, a concentration gradient is set up which can affect the observed cell emf. Such an altered potential will return to its original value rather quickly, the rate determined by diffusion of the ions involved, and if the solution be agitated, the polarization ought to be dissipated almost instantaneously. This possibility may be eliminated, since experiment has shown that potential changes are stable and reversible even if the electrolyte is agitated with a gas bubbler.

A second type of polarization involves a layer of material on the metal-solution interphase which is not free to move. A thin layer of oxide on the metal surface, for example, is immobile. When stress is applied, it may become distorted or disrupted. If it is disrupted, bare metal is exposed to the electrolyte and the metal may exhibit a different potential until the faults are healed. If the film is distorted, it offers a different potential barrier for the electrode reaction. Attempts to test this hypothesis have yielded negative results. Large changes in *p*H, which may affect the properties of an oxide film, do not affect the stress coefficient of potential. Experiments in the presence of various dissolved gases have likewise failed to indicate an important variable. A single careful experiment in an oxygen-free electrolyte also showed typical potential changes. However, the small amount of oxygen remaining in this electrolyte may have been sufficient to constitute a monolayer on the wire surface. Thus, the hypothesis that an oxygen or oxide film is responsible for the observed results cannot be completely excluded.

The results obtained with the quinhydrone and ferrous-ferric electrodes are interesting in this connection. For such electrodes, an exchange of electrons takes place on the surface and the metal merely carries electrons to or from the reactants if the reaction is allowed to proceed. For the other class of electrodes ($M \rightarrow M^{+n} + ne$), a positive ion must cross the interphase between metal and solution. Perhaps these two types of processes are affected differently by changes in the interphase induced by applied stress. The small transient change in potential of the ferrous-ferric electrode with high compressional stresses is conceivably due to heat of stretching which is quickly dissipated within the solution. No agitation was used in this experiment.

Conclusions

The stress-induced changes in the electrode potentials of silver and gold cannot be explained by thermodynamic considerations. Ionic polarization within the electrolyte may be excluded. The polarization probably involves distortion or disruption of a film at the metal-solution interphase.

Acknowledgment

The authors are indebted to Dr. C. S. Smith and Dr. W. D. Robertson for many stimulating discussions. Thanks are also due Mr. K. K. Ikeuye for preparing the photomicrographs in Fig. 9 and Dr. W. Bergmann for preparing the metal specimens.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the Journal.

REFERENCES

1. T. W. Richards and G. E. Behr, *Z. physik. Chem.*, **58**, 301 (1907).
2. W. H. Walker and C. Dill, *Trans. Faraday Soc.*, **11**, 153 (1907).
3. H. Endo and S. Kanazawa, *Sci. Repts. Tôhoku Imp. Univ.*, **20**, 124 (1931).
4. U. R. Evans and M. T. Simnad, *Proc. Roy. Soc.*, **188A**, 372 (1947).
5. L. Giulotto, *Nuovo cimento*, **13**, 220 (1936).
6. W. Spring, *Bull. classe sci., Acad. roy. Belg.*, 1066 (1903).
7. G. Tammann and C. Wilson, *Z. anorg. Chem.*, **173**, 156 (1928).
8. L. V. Nikitin and V. G. Sochevanov, *Metallurg*, **1**, 23 (1935).
   L. V. Nikitin, *Compt. rend. acad. sci. U.R.S.S.*, **17**, 107 (1937); *Zhur. Obshchei Khim. (U.S.S.R.)*, **9**, 794 (1939).
9. L. R. Gautam and J. B. Jha, *Proc. Indian Acad. Sci.*, **18A**, 350 (1943).
10. W. A. Patrick and H. B. Wagner, *Anal. Chem.*, **21**, 752 (1949).
11. L. W. Winkler, *Z. anal. Chem.*, **53**, 665 (1914).

Anodic Behavior of Iron in H_2SO_4[1]

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ABSTRACT

Various phenomena associated with the steady state of the cell Fe | $H_2SO_4(2N)$ | Pt are discussed with particular emphasis on the factors governing reproducibility. The formation of a brownish, gelatinous coat is observed, but its significance is obscure and it appears to have no direct effect upon transients produced by short off-times. An empirical equation has been found which represents the short off-time transients over a relatively wide voltage range. A discussion is given of the principal points that must be embodied in a theory describing the transient behavior of the cell. The part played by the charging of the usual double layer is demonstrated to be of little consequence in the observed transients.

Introduction

In order to understand the nature of the processes taking place at an electrode in solution it is often convenient to see how the system behaves when it is disturbed. Knowledge of the resulting transient behavior may then enable one to invent a reasonable mechanism for the electrode process.

Electrode transients may be conveniently produced by making or breaking a circuit which consists of an external emf, e.g., a lead storage battery, an external resistance in series, and the experimental cell itself. If the external resistance is high, then it will account for most of the potential drop and the current will remain approximately constant while the cell voltage may vary over a fairly wide range (say of the order of one or two volts). If the external resistance is low, the current decreases more or less rapidly from the value obtaining at the instant the emf is first applied, and a steady state is eventually reached wherein the current does not change appreciably with time. The steady state current may be considerably less than the initial current. During such a transient, the cell voltage will remain approximately constant, and this will usually be an advantage because the number of possible chemical reactions will probably be at a minimum. If, on the other hand, the current is held about constant, important steady state regions may be missed entirely because the transient path in the current-voltage diagram does not intersect the steady state locus. Therefore, one should be able to work at constant voltage if desired, or at constant current, or with some convenient constant external resistance, the actual choice being governed by the particular purpose of the experiment.

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Maintaining the electrode potentials constant is most easily accomplished by keeping circuit resistance to a minimum. Alternative methods, involving feedback mechanisms, have been tried, but do not give very rapid control [see Lamphere and Rogers(1) and the literature therein cited]. The low-external-resistance method does away with elaborate electronic devices and moving parts, and has the advantage of being almost instantaneous in operation. To be sure, it controls the voltage across the whole cell, but there is effective control over one electrode if the other electrode is a nonpolarizable one.

Transient electrode effects have been known since the time of Ostwald at least [see Bartlett(2) for some pertinent references to the literature before 1945]. The phenomena are of many different types, among which overshoot and oscillations are both conspicuous and mysterious. Various attempts at explanation have been made, but these have invariably been of a qualitative nature. Burton(3) constructed a theoretical system within which materials could diffuse and react, and he showed that concentrations in such systems could overshoot. Ferguson and Bandes(4) studied the cell Pt | $H_2SO_4(2N)$ | Pt and remarked that "the cathode overshoots its normal value at the start. The anode has never been observed to do this. It is probably due to a more rapid development of back emf at the anode which causes an excessive amount of the total applied potential to reach the cathode at these very low applied potentials." This is an inadequate explanation, because (*a*) no reason is given as to why the back emf develops more rapidly at the anode, and (*b*) no prediction is made of the time course of the overshoot nor even of how long it will last. Bartlett (2) surveyed the anodic transients for the cell Fe | H_2SO_4 | Pt, and found overshoot, oscillations of the relaxation type, and pulsations. These transients resemble those found in biological systems, and a comparison was

made in a subsequent article by Bartlett (5). For more recent literature on anode behavior, one should consult the various articles listed at the end of this paper, the subjects of which are corrosion (6), polarization (7), electrolytic polishing (8, 9), electrolytic rectification (10), periodic phenomena (11), and passivity (12).

In the present paper, we wish to report on the steady state characteristics of the cell Fe | H_2SO_4 (aq) | Pt, on observations of the anode surface with the aid of a microscope, and on the behavior of the cell current after it has been interrupted for a short time (less than 0.02 to 0.03 sec).

Apparatus

The circuit employed in these experiments is shown semipictorially in Fig. 1. In all transient experiments, the electrolytic cell consisted of a 600 ml Pyrex beaker containing 300 ml of an aqueous solution of sulfuric acid, into which were placed the two current electrodes and a reference electrode. No attempt was made to isolate the anode from the cathode because the cathode product, H_2, was also produced at the anode itself during off-time. Preliminary experiments were carried out in both air-saturated and oxygen-free solutions in order to determine the effects of dissolved oxygen on the overshoot phenomenon and on the formation of the brownish, gelatinous anode coat. No qualitative differences in overshoot were apparent, and microscopic observations failed to show any changes in the anode coat due to dissolved oxygen. Consequently, in the work to be reported the more convenient air-saturated solutions were used. Unless otherwise noted, the acid concentration was 1 mole per liter ($2N$) and the temperature was 25°C. The anode structure consisted of a vertical brass rod with an L-shaped piece of 99.7 per cent pure analytical iron wire 1.60 mm in diameter (Central Scientific Company) soldered into its lower end. Picein 105 covered the entire assembly except for the end cross-section, A, of the iron wire, which constituted the anode surface. The anode surface was made horizontal and facing upward in order to minimize convection in the immediate vicinity of the anode, and to facilitate the escape of hydrogen bubbles formed during off-time. The cathode, K, was a 0.005 in. thick platinized platinum sheet, 3.0 cm x 3.3 cm, supported by a brass rod which was covered with picein.

In most of the work, a 0.1 normal calomel half-cell was used as the reference electrode. To make sure that this was not a source of contamination, check experiments were made using as reference electrode a mercury-mercurous sulfate half-cell [Hg | Hg_2SO_4, $H_2SO_4(2N)$]. The plot of steady state current against anode-reference potential was found to be the same in the two cases, except that, as expected, the potentials with reference to the sulfate electrode were more negative by 0.27 v than the anode-calomel potentials. Furthermore, the response to interruption of the current for a short time was found to be precisely the same for the calomel electrode as for the sulfate electrode, provided the two systems had the same previous history (for details see below).

The cell geometry, i.e., the relative positioning of the anode, cathode, reference cell, and walls of the containing vessel, affects the cell current and the anode potential only insofar as it affects the resistance of the current path between anode and cathode and the IR drop between anode and reference cell. In Appendix I it is demonstrated that almost all of the solution resistance is contributed by the solution in the immediate vicinity of the small anode, so that the resistance of the current path

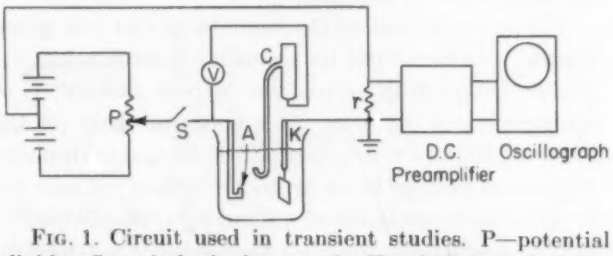

Fig. 1. Circuit used in transient studies. P—potential divider, S—switch, A—iron anode, K—platinized platinum cathode, C—0.1N calomel electrode, r—current resistor, V—vacuum tube voltmeter.

should be independent of the cell geometry, provided that the cathode area is large compared to that of the anode and the distances between anode and cathode, and between anode and walls of the containing vessel, are large compared to the dimensions of the anode. Similarly, the IR drop due to the solution resistance should be independent of cell geometry, provided that the distance between the anode and the reference electrode is large compared to the dimensions of the anode. As expected, the transient and steady state behaviors were found to be relatively independent of cell geometry.

Electrode potentials were measured with a Hewlett Packard model 410A vacuum tube voltmeter, V. Since this meter has a d-c input impedance of 100 megohms, the current drawn by it had a negligible effect on the reference cell and the potentials being measured. The meter had a rated accuracy of 3 per cent of full scale, and the one-volt scale could easily be read to a hundredth of a volt (estimated to a thousandth). Although this means of measuring electrode potentials lacks the accuracy of the potentiometric method, it was sufficiently accurate for our purposes and afforded convenience and rapidity of operation.

A continuously variable source of emf with the lowest possible internal impedance was required for the electrolyzing potential, the low impedance requirement being imposed by the desire to make the electrolyzing potential relatively independent of the cell current. The primary source of power consisted of eighteen 2-volt, heavy duty lead storage cells (Willard) arranged in two batteries of 9 parallel cells each, the two batteries being connected in series to give a voltage of 4 v. The resulting battery was connected across a potential divider, P, consisting of a 21 turn helix of $\frac{1}{16}$-in. x $\frac{1}{4}$-in. strap iron wound on a texolite cylinder 5 in. in diameter. The resistance of the potential divider was approximately 0.2 ohm at its operating temperature. This arrangement afforded a source of electrolyzing emf which could be varied continuously from -2 v to $+2$ v, and had a maximum output resistance of approximately 0.5 ohm with the moving contact of the potential divider set at its central position.

The current passing through the cell at any given instant was measured by recording photographically the potential drop across the current resistor, r, of approximately 0.3 ohm. This potential drop (of the order of 10^{-3} v) was preamplified by a d-c amplifier capable of voltage gains up to 2500, then fed into the horizontal d-c amplifier of a Dumont type 279 oscillograph. A specially designed 35-mm camera with film moving continuously in the vertical direction photographed the current deflection, thus recording cell current as a function of time. Since the camera was driven by a synchronous motor through a chain-drive, it provided a very linear and easily calibrated time base. A gear shifting mechanism in the camera permitted film speeds of 1, 5, 10, and 50 in. / sec. At the conclusion of each experiment, calibration of the current-measuring system was accomplished by passing known currents (determined by meters which had been checked against a silver coulometer) through the current resistor, r, and recording the resulting deflections on the film along with the transient data. In this way it was possible to eliminate all errors arising from nonlinearities in the amplifiers, the cathode ray tube, and the camera optics. The reduction of the photographic data was accomplished with the aid of a microfilm reader giving magnifications up to 13 diameters.

In earlier work (2) the switch, S, consisted of a hand-actuated SPST microswitch, which proved to be quite satisfactory in the study of long off-time phenomena. At off-times of the order of 0.1 sec and less, however, there was a tendency toward erratic behavior on the make at the end of off-time. This was attributed to contact bounce resulting from too vigorous actuation of the switch. The present transient studies required a switch giving continuously variable off-times with positive action on both the make and break. This requirement was met with a SPDT toggle type of switch designed to utilize the transit time of the pole between the two contacts as the off-time. The distance between the contacts could be varied continously to give off-times from less than 0.005 sec up to 0.035 sec. For work requiring precise cycling of the cell, i.e., the series repetition of a given off-time and on-time, it was necessary to construct a motor-driven switching device. Briefly, the motor-driven switch consisted of two cam-actuated microswitches, one of which initiated the off-time, the other terminated it. By separating the functions in this manner, it was possible to go to fairly short off-times with a minimum of contact bounce. The phase angle between the cams could be adjusted to give a continuous variation in off-time from 0.01 sec to 0.28 sec. Rheostats in series with the field and armature of the shunt-wound motor permitted continuous variation of the on-time from about 1 sec to approximately 3 sec.

Experimental

The Steady State

Once the electrode has reached the point where the current does not vary with time, it is relatively easy to make electrical and optical observations on it. For this reason, such observations will be discussed first.

When a freshly filed iron anode is placed in a solution of 1*M* H_2SO_4 it immediately assumes a potential of about -0.65 v with respect to a 0.1*N* calomel reference electrode. Then if switch, S, (Fig. 1) is closed (external circuit resistance 0.5 ohm) and potentiometer, P, is adjusted to give an anode-calomel potential of -0.65 v, no current will flow through the cell. If now the anode-calomel voltage is made more positive in steps of, say, 0.05 v, allowing at least one minute for the current to assume a steady value after each voltage change, the current vs. anode-calomel voltage curve will be as shown by curve A, Fig. 2. At -0.65 v there is vigorous gas evolution at the anode (presumably pure H_2 resulting from acid action). The gas evolution decreases steadily as the voltage is increased until at a voltage in the region of -0.4 v it is, for all practical purposes, completely stopped. Coincident with the cessation of gas evolution, the current drops to about one-third or one-fourth of its peak value, where it remains fairly constant as the voltage is increased to 0.08 or 0.09 v. At this voltage (very critical) periodic activity sets in. This activity consists of current bursts occurring at intervals depending markedly on the voltage, the repetition rate decreasing from the order of 100/min at 0.09 v to the order of 1/min at

0.13 v. At about 0.15 v the current pulses cease (or at least become less frequent than 1 per 5 min) and the current decreases gradually as the voltage is increased until at about 0.3 v it is negligibly small (less than 0.1 ma). The anode is now in the passive state, and no appreciable current flows with increasing voltage until 1.4 v is reached. At this voltage gas evolution begins at the anode (presumably pure O_2 resulting from electrolytic decomposition of water) and the current increases rapidly with increasing voltage.

If the previous procedure is now reversed by starting at the higher voltages and decreasing the voltage in steps, waiting for a steady state to be reached after each voltage change, the current vs. anode-calomel voltage dependence will be as shown by curve B, Fig. 2. The two curves are either coincident or nearly so for all voltages above approximately −0.2 v. At about −0.4 v the current rises slightly before decreasing with decreasing voltage, and gas evolution begins, increasing in vigor as the voltage is decreased. Increasing voltage always gives rise to curve A, while decreasing voltage gives rise to curve B. By running the voltage up and down rapidly between, say, −0.55 v and −0.1 v it is possible to describe repeatedly a closed loop in a current vs. voltage plot, the loop being bounded on the top by a curve such as A and on the bottom by a curve such as B.

From Fig. 2 it is seen that the behavior of the anode can be classified broadly according to the voltage region in which it is operating: below 0.08 v it is "active," above approximately 0.3 v it is "passive" and in the "transition" region, 0.08–0.3 v, pulsations occur. In this paper we are concerned primarily with the active region.

It should be pointed out that the current carried by an active anode is quite stable over a period of time (with an exception to be discussed below), and the anode will remain active indefinitely, *provided that the external resistance is very low and the source of electrolyzing emf is less than about 0.6 v on open circuit*. If the external resistance is appreciable, any polarization process that tends to reduce the cell current will also cause an increase in the voltage across the cell (because of reduced IR drop external to the cell). This increase in voltage may either initiate a new process or accelerate the original polarizing process, with the result that the current may be further reduced and the voltage further increased, eventually causing the anode to become passive if the anode-calomel voltage can exceed about 0.2 v. It is in this respect that the present technique differs essentially from those of previous workers. By making the external resistance very small, it is possible to make the anode-calomel potential relatively independent of the cell current, with the result that the anode can sustain indefinitely an apparent C.D. of the order of 200 ma/cm² without being passivated.

The curves of Fig. 2 are quite reproducible in the transition and passive regions, but somewhat less so in the active region. In any given experiment, the shape of the curves will be as shown in Fig. 2, but the exact values of the currents will differ somewhat from experiment to experiment.

Observations with Microscope

In the course of recent experiments employing a low power (65×) microscope to study the surface of the anode, certain phenomena were observed that may account for the lack of reproducibility in the active region.

In traversing curve A of Fig. 2, i.e., increasing the voltage from −0.65 v, one observes at the lower voltages, where gas evolution occurs, that the anode

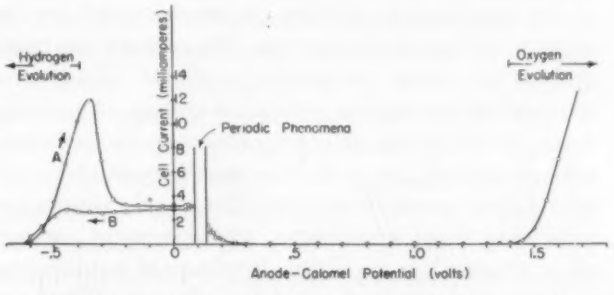

FIG. 2. Typical dependence of steady state current upon anode-calomel voltage. Anode area = 2.0 mm².

is metallic gray, badly pitted, and presents a very jagged appearance, with gas bubbles streaming profusely from the pits and surface. Near the peak of curve A, the anode begins to turn black. Coincident with this change there is a marked decrease in the gas evolution and the current begins to decrease with increasing voltage. At slightly higher voltages, the current becomes relatively independent of the voltage, the anode loses its jagged appearance, becoming relatively smooth, and the black coat gives way to a thick brownish coat. This brownish coat, because of its apparent effect on the stability and reproducibility of the steady state current in the active region, merits a more detailed description.

With an anode-calomel voltage of −0.2 v, the brownish coat seems to form first as a thin (probably less than 0.01 mm), transparent film covering the entire surface of the anode. Under the action of convection currents and occasional bubbles, this thin film soon (within a few minutes) rips in one or more places exposing a sizeable portion of the anode surface. The "flap" thus formed then folds or curls up in a loose roll that generally extends out from the anode surface approximately 0.1 mm. While this

process is going on, the intact portion of the layer seems to increase in thickness and irregularity, and black spots slowly form at random on the surface. Trapped bubbles occasionally break loose, carrying with them pieces of the layer, and now and then a piece falls away apparently as a result of the pull of gravity (probably aided by convection). As a result of this random growth, breaking up, and reagglomeration of the original layer, a ragged, irregular brownish coat is formed, having a gelatinous appearance, and a maximum thickness of the order of 0.1 mm. While this coat is being formed the cell current drops more or less steadily, until finally the coat, which appears to be impervious to the acid, reaches an equilibrium state wherein its rate of mechanical deterioration balances its rate of formation and the cell current becomes relatively steady. The time required for mechanical equilibrium of the coat to be established amounts to about 10–20 min. The removal of a portion of the coat by any of the above mentioned agencies is accompanied by an abrupt increase in the current, the current rise being greater the larger the portion removed. Thus, since the coat is undergoing continual change, the steady state current of the cell (with the anode active) consists of random (in both time and magnitude) variations about some fixed value. This fixed value varies somewhat from experiment to experiment, apparently depending upon the mechanical equilibrium configuration attained by the anode coat. Wherever the anode surface can be viewed through the brown coat, it appears to have a "swarming" motion, the appearance being somewhat analogous to that of a gray table top swarming with ants and viewed from a great distance. The volume in which this motion takes place lies close to the anode, probably extending out from the anode less than 0.01 mm.

At voltages immediately below the transition region, formation of the brown coat appears to stop, the coat (formed at lower voltages) loosens and becomes very susceptible to removal by convection, gravity, etc. With the coat's removal, the anode surface becomes relatively clear except for scattered black spots. The "swarming" appearance characteristic of the active region persists.

At voltages in the transition region, the appearance of the anode is much the same as it is at voltages slightly below the transition region except for an additional effect associated with periodic activity. With each burst of current, the surface of the anode appears to "twitch," the "twitch" apparently coinciding with the drop in current at the end of the current pulse. This "twitch" is probably best described as a brief change or discontinuity in the "swarming" motion characteristic of voltages in the active region, and appears to be confined to a volume extending out from the anode less than 0.01 mm. The "twitch" is propagated across the face of the anode, starting from the bottom in the case of a vertical anode. Coincident with each current pulse, small flakes of the black material previously formed on the anode are observed to fall away from the face of the anode.

When the voltage is raised to the point where the anode becomes passive, there are no "swarming" or "twitching" motions, and there is no coat or layer (so far as can be seen with 65× magnification) that is in a process of formation or deterioration—there are no visible signs of activity of any kind.

For every voltage region, the anode has such a definite and characteristic appearance that the voltage region in which it happens to be operating can be readily identified by direct microscopic observation of the anode surface alone.

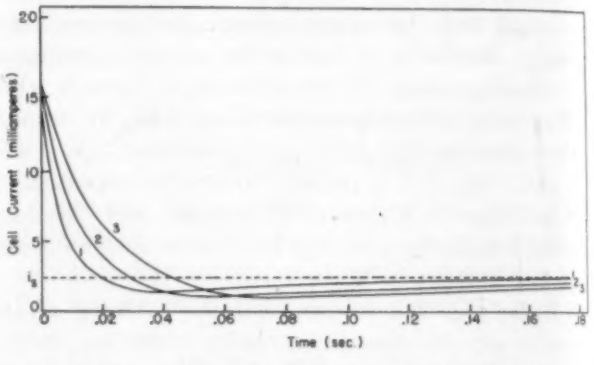

FIG. 3. Dependence of short off-time transients upon length of off-time. The off-times are: (1) 0.006 sec, (2) 0.009 sec, (3) 0.014 sec. Anode-calomel voltage = −0.2 v. Anode area = 2.0 mm².

Transients Produced By Total Switching

If the cell current is interrupted briefly, i.e., for less than approximately 0.03 sec, by opening and closing switch S, Fig. 1, while a steady state current is flowing, the current, after dropping to zero for the duration of the interruption, jumps to an initial value considerably greater than the steady state value, decays rather rapidly to a minimum somewhat lower than the steady state value, then rises slowly to the original steady state value. Typical curves for an active anode are shown in Fig. 3, time being reckoned from the end of the current interruption (off-time).

If, for a given off-time, the initial current, the steady state current, and the minimum current are plotted as functions of the anode-calomel voltage, a set of curves such as given in Fig. 4 is obtained. Thus, when the circuit is closed at the end of off-time, the current jumps initially to point a (Fig. 4), decays along the dotted line fairly rapidly to point b, then rises along the dotted line more slowly to

point c, the value of the steady state current before interruption. The time dependence of this current transient is shown in Fig. 3. It is to be noted that the i_s curve of Fig. 4 corresponds to curve B of Fig. 2, and that the cessation of overshoot[2] of the type shown in Fig. 3 appears to coincide with the beginning of gas evolution at about −0.4 v as the voltage is decreased and with the onset of periodic activity at 0.08 v as the voltage is increased. Since the maximum overshoot occurs about halfway between these two values, it was decided to conduct the transient studies with an anode-calomel voltage of −0.2 v.

It should be pointed out in passing that Fig. 4 can also be used to obtain information pertaining

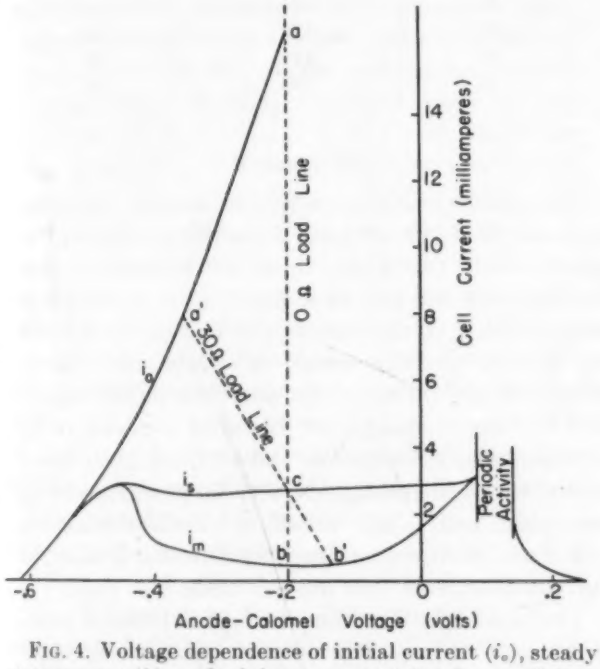

FIG. 4. Voltage dependence of initial current (i_o), steady state current (i_s), and minimum current (i_m) for an off-time of 0.03 sec. Anode area = 2.0 mm².

to the cell transients occurring when the circuit resistance is not negligible. By drawing a "load-line," corresponding to the circuit resistance, through the point representing the steady state, one can determine the initial current and, to a first approximation, the minimum current of the transient from the intersections a′ and b′, respectively. The time dependence of such transients is, however, more complicated than that shown in Fig. 3 and will not be discussed in this paper.

In order to obtain reproducibility of successive transients, it is found that the immediate history of the anode must be faithfully reproduced for each transient. This requirement can be met by cycling, i.e., the series repetition of a given off-time and on-time. As pointed out in the section on apparatus, cycling was accomplished in these experiments by means of a motor-driven switching device. Cycling, however, does not completely solve the problem, for it is found that transients resulting from off-times greater than about 0.03 sec still cannot be reproduced with a great degree of accuracy. Furthermore, although the individual transients in a series of, say, a dozen transients produced by short off-times are found to be exact reproductions of each other, they are not very accurate reproductions of transients recorded several minutes earlier or later. Partial clarification of the problem of reproducibility is to be found by examining the anode surface with a microscope.

Under a low power microscope (65×) it is seen that gas evolution begins immediately after the circuit is broken at the beginning of off-time, and ceases soon after the circuit is closed at the end of off-time. During off-time the gas bubbles play havoc with the brownish anode coat, tearing it, shifting it, and even removing it entirely if the off-time is great enough. Because of its loose and haphazard nature, the brownish coat never returns to the configuration it had before the current interruption. Therefore, it is not surprising to find that long off-time transients are not exactly reproducible. As the length of off-time is decreased, however, the disruptive effects of gas evolution also decrease. This is due to the fact that the bubbles act upon the coat for a shorter time and also because the gas evolution is less vigorous at the beginning of off-time. If the off-time is sufficiently short, no visible gas evolution occurs during the current interruption and the brownish coat on the anode appears to be unaffected. Under these circumstances it is found that the individual transients of a short series of transients are exact reproductions of each other, the variations occurring over longer series of transients apparently resulting from the slow, random changes characteristic of the brown coat.

It is important to note that overshoot manifests itself at the surface of the anode as a change in the "swarming" motion that is so characteristic of an active anode. The change, difficult to describe, is accompanied by an apparent change in the intensity and color of the light reflected from the surface of the anode, and appears to be in phase with the current transient as observed on the oscilloscope. These changes, intimately associated with the anode, are the only visible effects that a short off-time has at the anode surface.

As can be seen from Fig. 3, the length of the off-time has a marked effect upon the resulting transient. In particular, we note that the initial current,

[2] Experiments with an anode sleeve showed that convection does not exert an important influence on the overshoot phenomena described in this paper.

the minimum current, and the time required to reach the minimum current, all have a pronounced dependence on the off-time. These quantities are plotted as functions of off-time in Fig. 5 for a wide range of off-times.

A more complete description of the transients and their off-time dependence is afforded by an empirical equation of the form

$$i = Ae^{-k_1 t} - Be^{-k_2 t} + i_s \qquad (I)$$

where i is the cell current at time, t, after the end of off-time, and A, B, i_s, k_1, and k_2, are all positive

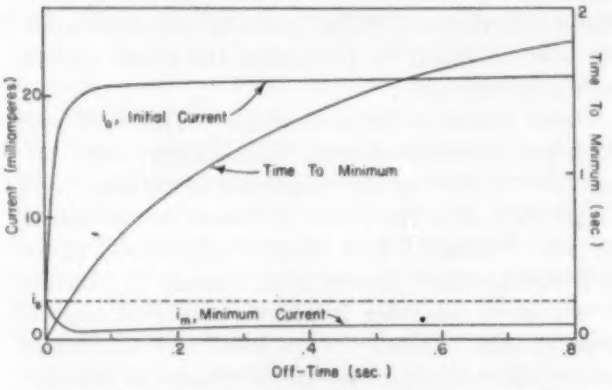

FIG. 5. Off-time dependence of initial current (i_o), minimum current (i_m), and time required to reach the current minimum, for an anode-calomel voltage of −0.2 v. Anode area = 2.0 mm².

TABLE I. *Values of constants appearing in equation (I), determined for an anode-calomel voltage of −0.2 v, and a temperature of 23°C. Anode area = 2.0 mm²*

Off-time (sec)	A (ma)	B (ma)	$C = i_s$ (ma)	k_1 (sec^{-1})	k_2 (sec^{-1})	$\frac{A}{k_1}$ (milli-coulomb)	$\frac{B}{k_2}$ (milli-coulomb)	$\frac{k_2 A}{k_1 B}$
0.006	13	1.6	2.1	128	21	0.10	0.076	1.3
0.009	17	3.4	2.1	67	15	0.25	0.23	1.1
0.014	21	7.1	2.3	40	14	0.53	0.51	1.0
0.018	18	3.4	2.4	36	7.0	0.50	0.49	1.0
0.023	20	3.9	2.2	35	6.6	0.57	0.59	1.0
0.026	20	3.7	2.0	32	3.4	0.63	1.1	0.6
0.035	20	3.5	2.0	35	6.4	0.57	0.55	1.0

quantities. The steady state current, i_s, is independent of off-time. The other quantities depend upon off-time and a statement of these dependences together with (I) constitutes a complete description of the transients at various off-times. Equation (I) is a very good representation of the transients occurring at all voltages where pronounced overshoot occurs and for all off-times less than about 0.03 sec. Typical values of the constants appearing in (I) are given in Table I as a function of off-time for an anode-calomel voltage of −0.2 v. These constants also show a marked dependence upon the anode-calomel voltage. Approximate values of k_1 and k_2 as functions of anode-calomel voltage are given in Table II for an off-time of 0.005 second.

The voltage dependences of i_s and of

$$i_o = A - B + i_s$$

are given in Fig. 4. The temperature dependences of these constants have not been studied in detail as yet.

TABLE II. *Dependence of k_1 and k_2 upon voltage for an off-time of 0.005 sec and a temperature of 23°C*

Anode-calomel voltage	k_1 (sec^{-1})	k_2 (sec^{-1})
−.40	94	—
−.35	110	—
−.30	94	—
−.25	129	21
−.20	178	26
−.15	483	14

DISCUSSION

The above results give rise to several questions, to some of which at least a partial answer can be given, while for others there are indications that further work will lead to a quantitative explanation. Among other things, one would like (*a*) to account for the observed dependence of steady state current upon voltage, (*b*) to predict what the initial current and its rate of change will be, after a period of interruption, as a function of the off-time, (*c*) to know under what circumstances overshoot will occur at an anode, and (*d*) to obtain a kinetic description which will allow a quantitative prediction of how the current transients will depend upon the time.

The clue to the direction in which to proceed seems to be provided by experiments, which were made subsequently to those reported above, on the behavior of a copper anode in hydrochloric acid. In this case it has been shown that the transient behavior is due to the formation of a resistive layer, presumably cuprous chloride. Since the phenomena observed for iron in sulfuric acid are to a great extent similar to those found for copper in hydrochloric acid, it is natural to suppose that there is a resistive layer on the iron anode. The central problem then is to determine how this resistive layer is formed or removed, and this problem can be attacked profitably by electrical or optical methods, or both.

The observed transient currents cannot be attributed to the charging or discharging of the usual electrical double layer. From Table I, we see that the transient charge is 5×10^{-4} coulomb = 15×10^{5} esu. This corresponds to the charge on 3×10^{15} singly charged ions. Assuming an ion to occupy a minimum volume of 3×10^{-23} cm³, this number of

ions would occupy a volume of at least 10^{-7} cm³. Since the anode has an area of 0.02 cm², a layer would have to be 5×10^{-6} cm thick, or 300 ions deep, at the minimum. Such a layer would have a thickness considerably greater than that ordinarily attributed to double layers. An even more striking argument concerns the decay time of the transient. Assuming an electrode capacity of 10 μf/cm², the capacity of the anode is 0.2 μf. Since the circuit resistance is only of the order of one ohm, the time constant is 0.2 μsec, and the charging transient is over in 10^{-6} seconds. The transients studied in this paper require 10^{-1} seconds or more for completion.

The internal resistance, r, of the cell (from anode to calomel) may be found by means of interruption experiments. The anode-calomel potential, V, may be regarded as made up of three parts: (*a*) the potential for zero current, (*b*) the overvoltage, and (*c*) the ohmic potential drop. We shall lump (*a*) and (*b*) together as $\epsilon(i)$, so that $V = \epsilon(i) + ir$. The decay of the ohmic potential takes place in less than a microsecond (13), while the value of $\epsilon(i)$ decreases at a much slower rate. In the copper system, there is a very clear-cut separation of these two decays. The change in $\epsilon(i)$ appears to be due mainly to changes in the nature of the anode layer, although there may be some contribution from diffusion effects. Further studies need to be made on iron, but one can say that for *active* iron, $\epsilon(i)$ decays rapidly and that the ohmic drop is quite evident, but that for *passive* iron $\epsilon(i)$ changes more slowly and seems to mask completely any ohmic drop.

Interruption experiments may enable us to find how the electrode potential, ϵ, and the resistance, r, vary as a function of time. The value of i_s will be determined by what ϵ and r are at the time the circuit is remade. From Fig. 5, it is seen that the value of i_s has become steady after 0.1 sec. This may mean that both r and ϵ have reached their steady values, but this needs to be confirmed by special experiments.

Flow of Charge

Since the steady state current is not a contributor to the building-up of the layer, we shall consider the effect of the current $i - i_s$. If we integrate equation (I) with respect to time, we have

$$\int_0^\infty (i - i_s)\,dt = -(A/k_1)e^{-k_1 t}\Big|_0^\infty + (B/k_2)e^{-k_2 t}\Big|_0^\infty = (A/k_1) - (B/k_2) \qquad \text{(II)}$$

The first term on the right-hand side is the amount of charge which flows into the solution from the anode and the second term is the amount of charge which flows (more slowly) in the opposite direction. From Table I, it is seen that these two amounts of charge are equal, and that the total charge which flows ($\int i\,dt$) equals the charge which would flow if the system were in the steady state ($\int i_s\,dt$). The physical basis for this is still obscure.

Formation and Removal of the Layer

The construction of an adequate kinetic description of the anode phenomena which we have observed seems to hinge on knowing how the resistive layer can be formed and later removed. In the copper system, for moderate external resistance, growth of the layer usually starts at random spots (ridges) on the anode and is a sideways affair. (This has been demonstrated by cine photomicrography at the rate of 64 frames/sec.) However, when $R = 0$, the current vs. time curve indicates that the layer is growing in depth (thickness). Further experiments with rapid photography of the surface should show precisely what happens, and should in particular answer the question as to just how overshoot occurs, and whether or not it is linked with sideways growth.

When the applied field is removed, the layer comes off, both in iron and in copper. This has been studied more thoroughly in copper, where it is observed that, after interruption, ϵ remains approximately constant (is on a plateau) for a while and then drops in a sharp S-curve to a new value. The time spent on the plateau is greater the greater the initial value of the voltage. One might suppose that this electrical change is correlated with dissolving of the layer by the acid, but this is not borne out by visual observation, which shows that the layer seemed to remain intact for at least two seconds in one case, while the electrical change was completed in about 0.05 sec. This electrical change is accompanied by a sudden whitening, which may be due to some sort of Kerr effect.

The steady state will be reached when the reactions tending to form the layer are proceeding at a rate equal to that of the reactions tending to remove the layer. These in turn depend on the concentrations of the various ions or molecules present, and the rates of supply of these must be equal to the rates of removal.

The general subject of formation of layers on surfaces has received a good deal of attention (14–17), both experimentally and theoretically. The present work stresses the importance of further development in this field, and it seems fairly certain that this will bring definitive and complete answers to the questions raised at the start of this discussion.

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APPENDIX I

An interesting property concerning the solution resistance between two electrodes can be demonstrated by first considering the simple case of two concentric spherical electrodes having radii a and b, with an electrolyte of specific resistivity ρ between them. Clearly, the total resistance between the electrodes is just the sum of the resistances of spherical shells of thickness, dr, where the resistance of one such shell is

$$(dR)_r = \frac{\rho dr}{4\pi r^2}.$$

Thus, the total resistance between a and b is just

$$R_a^b = \int_{r=a}^{r=b} (dR)_r = \int_a^b \frac{\rho dr}{4\pi r^2} = \frac{\rho}{4\pi a}\left[1 - \frac{a}{b}\right].$$

As the radius of the outer electrode becomes large compared to that of the inner electrode, the total resistance approaches the finite value $(\rho/4\pi a)$.

Now let us consider the resistance between two widely separated (nonconcentric) spheres, having radii a and a', which are immersed in an electrolyte of specific resistivity ρ. From the above result, the resistance contributed by sphere a will be $O(\rho/4\pi a)$, that is, "of the order of" $(\rho/4\pi a)$, and that contributed by sphere a' will be $O(\rho/4\pi a')$. The total resistance will, therefore, be

$$R_a^{a'} = O\left(\frac{\rho}{4\pi a}\right) + O\left(\frac{\rho}{4\pi a'}\right).$$

In the case where $a \ll a'$, $O(\rho/4\pi a) \gg O(\rho/4\pi a')$, and we get the interesting result that

$$R_a^{a'} = O\left(\frac{\rho}{4\pi a}\right).$$

Thus, the solution resistance between two widely separated spherical electrodes, one of which is much smaller than the other, depends only on the size of the smaller electrode and not upon the separation of the electrodes. The major portion of this resistance is contributed by the solution lying within a sphere concentric with the smaller electrode and having a radius $\sim$10 times that of the smaller electrode. Evidently this result can be generalized to include electrodes of arbitrary shape, provided only that the dimensions of one of the electrodes are much smaller than those of the other, and that the separation of the electrodes is large compared to the dimensions of the smaller electrode.

Summary

1. Various phenomena associated with the steady state in the cell Fe | $H_2SO_4(2N)$ | Pt have been discussed with particular emphasis on the factors governing reproducibility. The formation of a brownish, gelatinous coat is observed, but its importance is obscure, and it appears to have no direct effect upon transients produced by *short* off-times.

2. An empirical equation has been found which represents the short off-time transients over a relatively wide voltage range.

3. The transients are discussed using the assumption that a resistive layer is primarily responsible for them. The formulation of the kinetics of the formation and removal of such a layer appears to require extensive optical experimentation.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the Journal.

REFERENCES

1. R. W. Lamphere and L. B. Rogers, *Anal. Chem.*, **22**, 463 (1950).
2. J. H. Bartlett, *Trans. Electrochem. Soc.*, **87**, 521 (1945).
3. A. C. Burton, *J. Cellular Comp. Physiol.*, **14**, 327 (1939).
4. A. L. Ferguson and H. Bandes, *Trans. Electrochem. Soc.*, **81**, 273 (1942).
5. J. H. Bartlett, *J. Cellular Comp. Physiol.*, **32**, 1 (1948).
6. J. J. Lander, *J. Electrochem. Soc.*, **98**, 213 (1951).
7. D. R. Turner, *J. Electrochem. Soc.*, **98**, 434 (1951).
8. H. F. Walton, *J. Electrochem. Soc.*, **97**, 219 (1950).
9. U. R. Evans, "Metallic Corrosion, Passivity and Protection," pp. 614–616, Edward Arnold and Co., London (1946).
10. H. E. Haring, *J. Electrochem. Soc.*, **99**, 30 (1952).
11. H. Lal, H. R. Thirsk, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **47**, 70, 999 (1951).
12. K. F. Bonhoeffer, *J. Gen. Physiol.*, **32**, 69 (1948); U. F. Franck, *Z. Naturforsch.* **4a**, 378 (1949); K. F. Bonhoeffer and U. F. Franck, *Z. Elektrochem.*, **55**, 180 (1951).
13. S. Schuldiner and R. E. White, *J. Electrochem. Soc.*, **97**, 433 (1950).
14. N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Chap. VIII, Oxford University Press, London (1940).
15. U. R. Evans, *Trans. Faraday Soc.*, **41**, 365 (1945).
16. W. J. Moore and J. K. Lee, *Trans. Faraday Soc.*, **47**, 501 (1951).
17. N. F. Mott, *Reports of Progress in Physics*, Physical Society of London, **12**, 163 (1949).

The Electrochemical Behavior of Aluminum

III. In Buffered and Alkaline Solutions of Potassium Ferricyanide and in Sodium Hydroxide[1]

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ABSTRACT

A study has been made of the reactivity and polarization characteristics of pure aluminum in buffered and alkaline solutions of potassium ferricyanide and in sodium hydroxide. Electrode potentials, weight loss data, and polarization curves are presented; it is shown that the reaction of aluminum with these electrolytes may be interpreted from an electrochemical point of view. The analysis of the polarization behavior is based on the theory of the "mixed potential."

Introduction

This work is a continuation of a general investigation on the electrochemical behavior of aluminum in solutions containing oxidation-reduction systems (1). The present study involves buffered and alkaline solutions of potassium ferricyanide and sodium hydroxide; the experimental approach and the interpretation of the data follow along the same lines as those previously developed. Although the theory of the "mixed potential" has already been treated in some detail (1), the curves shown in Fig. 1 are presented in order to facilitate the interpretation of the experimental results reported. The curves f_c and f_a in this figure are what we call the "real" polarization curves for the cathodic reaction and the anodic reaction, respectively. These curves include portions which are sometimes designated self-polarization curves (2). The open circles and dashed curve are an experimentally obtained polarization curve on this system and what we call the "external polarization curve." I_a and I_c are the externally applied anodic and cathodic currents, respectively, i_a is the total anodic current and i_c the total cathodic current.

Experimental

Materials and apparatus.—Pure aluminum (99.99) in the form of rolled sheet (0.25 mm thick) was used in the experiments. All the solutions were made up with redistilled water and reagent grade chemicals: the compositions are given in Table I. The apparatus and the experimental conditions were identical to those previously given (1) except for the experiments in strong alkaline solutions and the temperature control. Since the dissolution rate of the aluminum is relatively high in these latter solutions, larger volumes of solution (one to two liters) were used in open beakers. All of the experiments were run at room temperature which was generally 26°C ± 1°C.

Procedure.—The aluminum was polished with #0000 paper using a kerosene paraffin mixture, cleaned in a hot mixture of alcohol and acetone and then in redistilled water. Great care was taken not to leave any abrasive particles imbedded in the surface. All but a defined area of about 1.0 to 2.0 cm² was coated with an insulating lacquer. In some of the weight loss experiments the exposed area was as much as 10 cm².

In general the experimental procedure was the same as previously used (1). Aluminum specimens were submitted to external polarization, and the electrode potential and external current density recorded. Bright platinum electrodes of the exact shape and size as the aluminum electrodes were placed in the cell in exactly the same position and polarized in order to obtain the limiting diffusion current of the oxidation-reduction system in each solution.

The "real" polarization curves for the reduction of $K_3Fe(CN)_6$ on aluminum and the dissolution of the aluminum were obtained by the weight loss method as follows: for any given solution a series of aluminum specimens were used; each specimen was polarized at a predetermined constant potential for a given time. The potential was held constant by means of a potentiostat, and the external current recorded by both a milliammeter and coulometers. At the end of the experiment the weight loss of the aluminum was determined. Since, at a constant potential, the external polarizing current initially varies rather rapidly with time finally becoming constant, the time of exposure was chosen so that the current I was approximately constant for about 90 per cent

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of the time. The actual value of I used was obtained from the coulometers. The results were interpreted as follows: for any given electrode potential, the external current density gives I_c or I_a, depending upon whether the specimen was cathodically or anodically polarized; the weight loss corresponds to i_a, and $i_c = i_a \pm I$, where the plus sign is for external cathodic polarization and the negative sign for external anodic polarization. These values were used to construct the "real" polarization curves for the system.

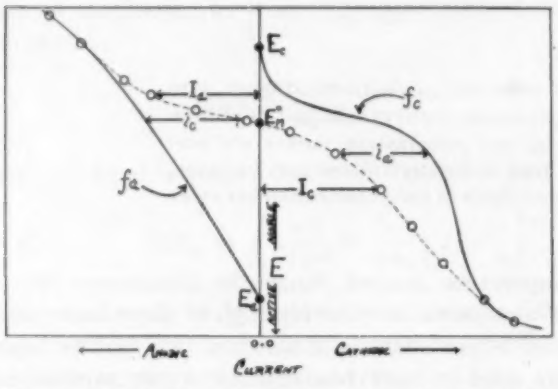

FIG. 1. Polarization curves for an "active" metal and an oxidation-reduction system. (See text for explanation.)

TABLE I. *Solution Composition*

Solution	$K_3Fe(CN)_6$* moles/l	Supporting electrolyte	pH
		Buffer	
1	0.25	HAC NaAC	3.4
2	0.25	HAC NaAC	8.3
		Buffer	
3	0.25	H_3BO_3 NaOH	9.3
4	0.25	H_3BO_3 NaOH	10.0
5	0.25	H_3BO_3 NaOH	10.8
6	0.25	H_3BO_3 NaOH	11.5
7	0.25	0.1*N* NaOH	—
8	0.50	0.1*N* NaOH	—
9	0.50	0.25*N* NaOH	—
10	0.50	0.50*N* NaOH	—
11	0.0	0.10*N* NaOH	—
12	0.0	0.25*N* NaOH	—
13	0.0	0.50*N* NaOH	—

* In most solutions there was an equivalent amount of $K_4Fe(CN)_6$ present.

Open-circuit potentials are designed as E^0, and all currents are given as current density per square centimeter of apparent surface area.

All values of electrode potentials are given with reference to the saturated calomel electrode.

RESULTS

Behavior in buffered solutions of $K_3Fe(CN)_6$; *pH 3.5 to 11.5.*—Solutions 0.25*M* in $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were buffered with HAC and NaAC or H_3BO_3 and NaOH in order to obtain solutions in the *p*H range of about 3.0 to 12.0. In all cases the total buffer concentration was about 1.0*M* and served also as a supporting electrolyte.

The open-circuit potential of platinum, E^0, was +0.24 v in all solutions containing equal concentrations of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, and +0.05 v in those which only contained $K_3Fe(CN)_6$. The limiting current densities $(I_c)_d$ and $(I_a)_d$ on the platinum electrode varied somewhat in the different solutions. All values, however, were very close to 6.0 ma/cm², except for solutions 5 and 6, where they were about 7.0 ma/cm² and 9.0 ma/cm², respectively. The exact values obtained in each instance are not reported, since approximate values suffice for the purpose of comparison with the results obtained on aluminum.

Generally, any one aluminum specimen assumed a fairly steady open-circuit potential, E^0, within ten to twenty minutes; there was, however, a variation from one specimen to another. Except for solutions whose *p*H was 10 or less, these variations amounted to only a few centivolts. At *p*H of 10 or less, E^0 assumed a value between +0.2 v and −0.2 v. At *p*H 10.8, E^0 was about −0.65 v while at *p*H 11.5 it was about −0.75 v.

When aluminum was cathodically polarized after the steady potential had been established in solutions 1 through 4, the limiting current density, l.c.d., for the ferricyanide reduction was very low, in some cases of the order of μa/cm². It was found, however, that if the polarization was performed rapidly and as soon as possible after the specimen was immersed in the solution, a matter of one or two minutes, a well-defined curve could be obtained with an l.c.d. of as high as 5.5 ma/cm² in some cases. Subsequent polarizations showed that the l.c.d. decreased rather rapidly with time reaching a value of the order of μa/cm² as a limit.

The results obtained in solution 3 (*p*H 9.3) are shown in Fig. 2; these curves are typical of the behavior in solutions 1 through 4. Generally, all specimens showed about the same behavior in solutions 3 and 4; whereas, in solutions 1 and 2 the l.c.d. on immediate immersion varied considerably from one specimen to another. In these latter solutions the limiting current density was never found to be as high as those at the higher *p*H, and the rate of its decrease with time was much greater, reaching the order of magnitude of μa/cm² in less than one hour.

At *p*H of 10.8 and 11.5, well-defined cathodic polarization curves for the reduction of ferricyanide were obtained. The curve and the l.c.d. were constant with time, and reproducible. The l.c.d. was about the same as that obtained on platinum, 7 ma/cm², in solution 5, and 8 ma/cm² in solution 6. A typical

result obtained at pH 11.5 is shown in Fig. 3. It may be seen that the curve obtained 19 hours after immersion is practically identical to the one obtained 30 minutes after immersion.

It was not possible to detect any change in the appearance of the aluminum surface by visual means after it had been exposed to the buffer solutions, and either allowed to remain at open circuit or cathodically polarized.

When the aluminum is anodically polarized in any of these solutions, the current begins to rise at about +1.0 v, reaches a maximum at about +1.5 v and then rapidly decreases to very low values at about +2.0 v. The maximum value was dependent somewhat on the particular specimen and the pH, but

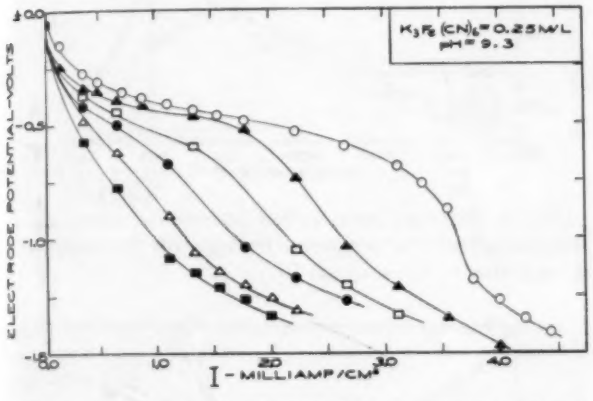

FIG. 2. External cathodic polarization curves for aluminum in solution 3. ○—2 min after immersion; ▲—26 min after immersion; □—45 min after immersion; ●—63 min after immersion; △—112 min after immersion; and ■—183 min after immersion.

in general it was in the neighborhood of about 1.0 to 2.0 ma/cm². At +2.0 v the current fell to only a few μa/cm².

Some experiments were run in pure buffer solutions without the presence of ferricyanide and ferrocyanide. The general behavior was the same, except that the maximum values were somewhat higher. Weight loss measurements in the vicinity of the maximum current indicate that the anodic reaction does not involve the dissolution of aluminum to any appreciable extent.

Anodic polarization in the range +2.0 v to about +3.0 v produced a definite film on the surface. The film is mostly white and opaque, but has some interference tints present. If the aluminum is cathodically polarized after it has been anodically polarized as above, the cathodic curve for the reduction of ferricyanide is not obtained. The curve hugs the voltage axis (practically zero external current) until the reduction of hydrogen occurs. This was found to be true, even after the aluminum had remained in the solution for 2 days.

By assuming that the E vs. i_a relationship in solution 6 is linear from open-circuit potential to about −0.3 v and extrapolating the external anodic polarization curve back to the voltage axis, the i_a at E^0, which is equal to the "local" action current i_o, was found to be about 0.35 ma/cm². Weight loss measurements gave 0.36 ma/cm² ± 0.01 ma/cm², showing close agreement.

Analysis of the polarization curves obtained for the reduction of ferricyanide on aluminum shows that $i_a \ll I_c$ so that $I_c \cong i_c$ and that the potential-current density relationship is given by:

$$E = b \log [(i_c)_\delta - i_c]/i_c - E^1/_2 \qquad (I)$$

where b is about 0.2 v and $E^1/_2$ varies to some extent with solution composition. For solutions 5 and 6 it is about −1.0 v.

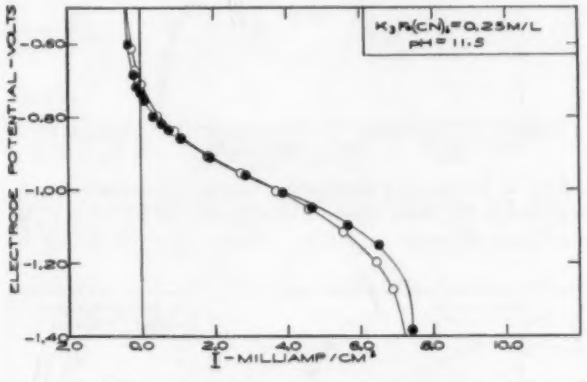

FIG. 3. External polarization curves for aluminum in solution 6. ○—30 min after immersion; ●—19 hr after immersion.

Behavior in solutions of $K_3Fe(CN)_6$ NaOH.—The concentration of $K_3Fe(CN)_6$ was either 0.25M or 0.50M while the NaOH was varied from 0.1M to 0.5M. Since it was determined quite early in the work that the presence or absence of $K_4Fe(CN)_6$ did not have any noticeable effect on the results, it was omitted from some of the solutions. As would be expected, the pH range of these solutions was from 13.0 to 13.70. The l.c.d. for the oxidation of ferrocyanide and the reduction of ferricyanide on bright platinum were more or less independent of the NaOH concentration and approximately equal. The l.c.d. was about 10 ma/cm² for 0.25M $K_3Fe(CN)_6$ and about 20 ma/cm² for 0.50M $K_3Fe(CN)_6$.

The open-circuit potential of aluminum becomes steady in a relatively short time in all of the solutions. Its value was dependent upon both the concentration of $K_3Fe(CN)_6$ and NaOH. Generally, an increase in NaOH tends to give a more anodic potential, whereas, an increase in $K_3Fe(CN)_6$ has the opposite effect. Thus, for a given concentration of NaOH (0.1N) the potential changes from about −1.0 v to −0.8 v with increase in $K_3Fe(CN)_6$ from

0.25 mole/l to 0.50 mole/l. While for a given concentration of $K_3Fe(CN)_6$ (0.5 mole/l) the potential changes from about −0.8 v to about −1.4 v with an increase of NaOH from 0.1*N* to 0.5*N*.

Aluminum assumes an E^0 of about −0.95 v in solution 7 (0.1*N* NaOH) with no indication of hydrogen evolution on open circuit. When the aluminum is cathodically polarized, evolution of hydrogen begins at about −1.5 v. While on open circuit, the surface becomes covered with a thin, iridescent film.

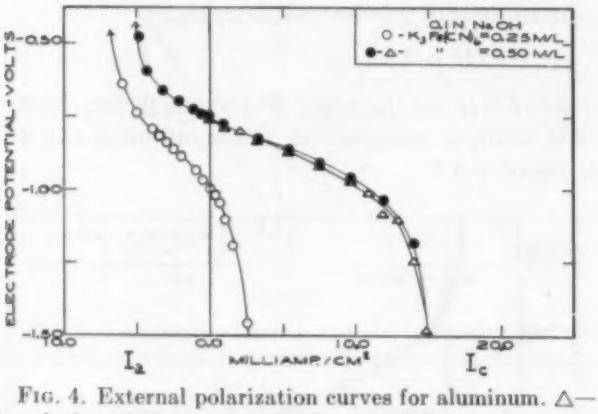

FIG. 4. External polarization curves for aluminum. △—In solution 10, from open circuit potential to −1.5 v; ●—in solution 10, from −1.5 v to −0.50 v; ○—in solution 9.

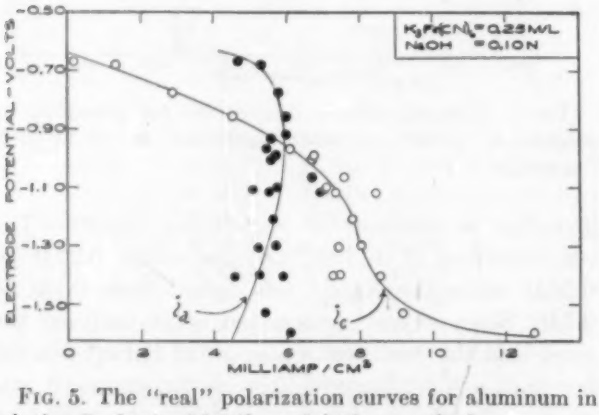

FIG. 5. The "real" polarization curves for aluminum in solution 7, obtained by the weight loss method.

On a few specimens a white, opaque film was noticed at localized areas. The thin, iridescent film appears to thicken when the aluminum is anodically polarized becoming white and opaque at about − 0.65 v, when a state of extreme polarization sets in where the potential becomes very noble (>+2.0 v) for a very small increase in current. A typical external polarization curve for this solution is shown in Fig. 4.

The shape of the polarization curve indicates strongly that it represents the cathodic reduction of ferricyanide, therefore suggesting that the "self-anodic" polarization curve (*E* vs. i_a) for aluminum in this solution from about −0.65 v to about −1.5 v is very close to a straight line and that i_a is approximately a constant with a value of about 6 ma/cm². With this interpretation the l.c.d. for the reduction of ferricyanide is about 8 ma/cm².

Polarization experiments by the weight loss method confirmed the above interpretation; a typical result is shown in Fig. 5. It may be seen that the *E* vs. i_a relationship is approximately linear and that i_a varies from about 5 ma/cm² at −1.5 v to about 6.0 ma/cm² at −0.7 v when it begins to fall very rapidly.

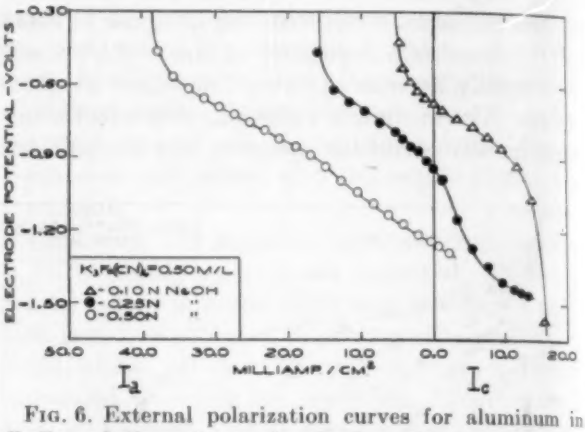

FIG. 6. External polarization curves for aluminum in alkaline solutions of potassium ferricyanide. △—solution 8; ●—solution 9; ○—solution 10.

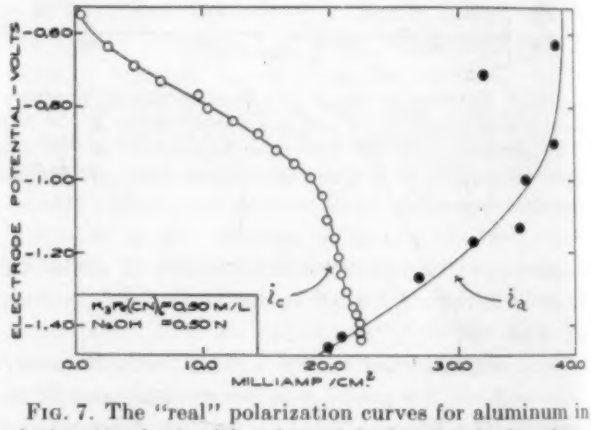

FIG. 7. The "real" polarization curves for aluminum in solution 10, obtained by the weight loss method and external polarization.

Except for specific effects due to the increase in $K_3Fe(CN)_6$ concentration, the results obtained in solution 8 are very similar to those given above. Typical results are given in Fig. 4 and 6. The open-circuit potential was about −0.75 v, and well-defined and reproducible polarization curves were obtained. The l.c.d. for the reduction of ferricyanide was approximately the same as that on platinum, 20 ma/cm².

An external polarization curve obtained in solution 9 is given in Fig. 6. As in the previous solutions, there is a strong indication that the *E* vs. i_a relationship is approximately linear, with i_a practically constant at about 16 ma/cm². On this basis the l.c.d.

for the reduction of ferricyanide is about 20 ma/cm² and again approximately equal to that on platinum.

In solution 10 the open-circuit potential is about −1.45 v and evolution of hydrogen was noticeable on the surface. The surface was evenly and uniformly etched and no film formation was apparent at potentials more anodic than about −0.5 v. Actually, the surface was brightly polished when submitted to external anodic polarization. At potentials more noble than about −0.5 v, a white, opaque film formed and the current density decreased rapidly. Some external polarization curves and "real" polarization

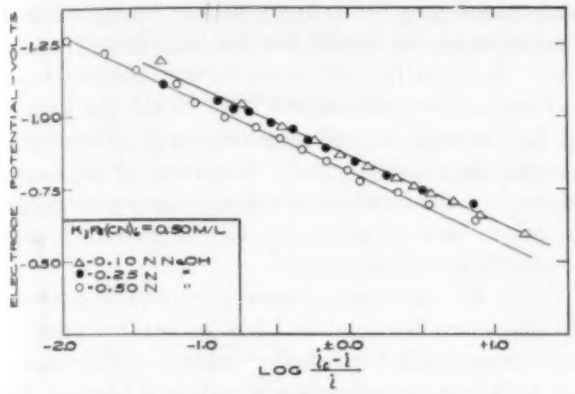

FIG. 8. The "real" polarization curve for reduction of ferricyanide on aluminum. △—solution 8; ●—solution 9; ○—solution 10.

TABLE II. *Variation of E½ and b with degree of alkalinity* [$K_3Fe(CN)_6$ = 0.50 mole/l]

Supporting electrolyte	*E*½ volt	*b* volt
0.1*N* NaOH	−0.85	0.22
0.25 NaOH	−0.86	0.22
0.50 NaOH	−0.82	0.23
Buffer		
*p*H ≅ 11	−1.0	0.23

curves obtained by the weight loss method are shown in Fig. 6 and 7.

In all cases the l.c.d. for ferricyanide is about 20 ma/cm² and approximately equal to that obtained on platinum.

It is interesting to note that in this solution the cathodic polarization curve for the reduction of ferricyanide on aluminum is obtained by an external anodic polarization.

The *E* vs. i_c relationship for the "real" cathodic polarization curve for the reduction of ferricyanide on pure aluminum in these solutions is of the same form as that in the buffered solutions given above: see equation (I). A typical set of curves is shown in Fig. 8 and the values of the constants in Table II.

Behavior in NaOH.—Polarization curves and weight loss data at constant potentials were obtained in 0.1*N* NaOH, 0.25*N* NaOH, and 0.50*N* NaOH. In these solutions the cathodic reaction is limited to the reduction of hydrogen. The reduction of oxygen no doubt also occurs but must be of a relatively small order of magnitude, since there was no appreciable difference in the results when nitrogen was passed through the solution.

Generally, the open-circuit potential in these solutions becomes fairly steady within about 30 minutes and is in the neighborhood of −1.6 v. There is a

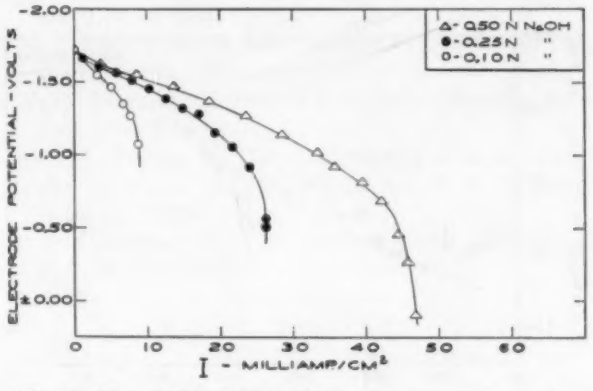

FIG. 9. External anodic polarization curves for aluminum in NaOH.

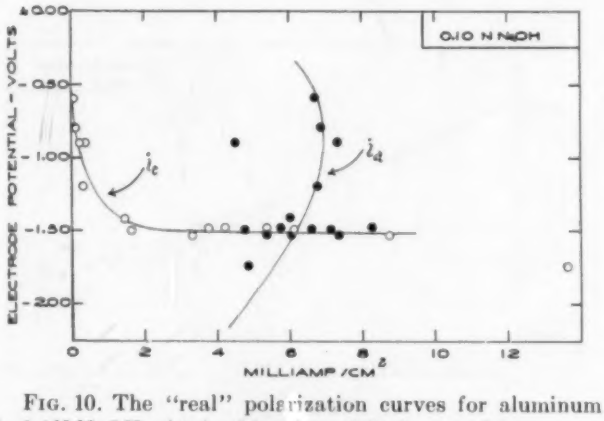

FIG. 10. The "real" polarization curves for aluminum in 0.1*N* NaOH, obtained by the weight loss method.

fairly rapid evolution of hydrogen on the surface on open circuit, which continues at a decreasing rate as the aluminum is anodically polarized. It finally disappears at about the potential at which visible film formation becomes evident. This latter point depends upon the concentration of NaOH. The surface becomes uniformly etched but remains fairly smooth and bright until the anodic polarization curve seems to reach a limiting current density at which point the rate of change of current with potential becomes negligibly small. In this region the surface first acquires a thin, iridescent film which rapidly seems to thicken showing strong interference colors. This anodic l.c.d. is about 8 ma/cm² for 0.1*N* NaOH, 25 ma/cm² for 0.25*N* NaOH, and about

45 ma/cm² for 0.50*N* NaOH, practically a linear relationship. Although the exact potential at which this phenomena occurs depends somewhat on the solution and particular specimen, it is generally at about −1.0 v. The curves in Fig. 9 show a typical behavior.

Although any one specimen gives well-defined polarization curves and open-circuit potentials, the results obtained with different specimens in the same solution show a variation of as much as 20 per cent. This is also true of the weight loss. This amount of

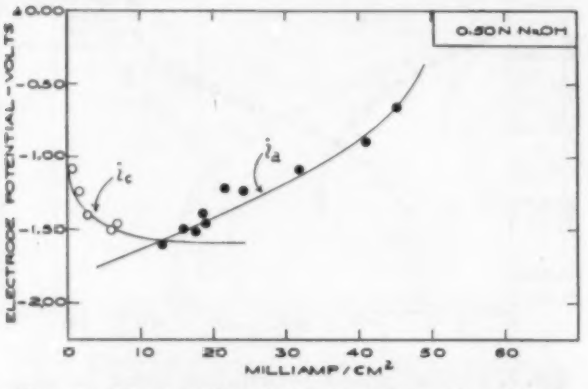

FIG. 11. The "real" polarization curves for aluminum n 0.5*N* NaOH, obtained by the weight loss method.

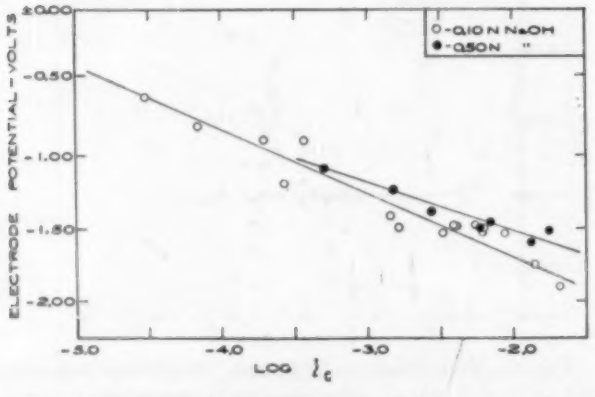

FIG. 12. The "real" cathodic polarization curve on aluminum in NaOH.

deviation about a mean is not surprising when due consideration is given to the rapid dissolution of the aluminum with the accompanying rather vigorous hydrogen evolution, in these solutions.

The "real" polarization curves for the dissolution of aluminum and the cathodic reduction of hydrogen were constructed by the weight loss method and typical results are shown in Fig. 10 and 11.

Generally, the values of i_c obtained from the "real" polarization curve for the reduction of hydrogen approximately fitted the usual hydrogen overvoltage relationship:

$$E = b_H \log i_c + \text{Const.}$$

Typical results obtained in 0.1*N* NaOH and 0.5*N* NaOH are shown in Fig. 12.

Discussion

The experimental results indicate that the reaction of aluminum in buffered and alkaline solutions of $K_3Fe(CN)_6$ and in NaOH may be interpreted by the theory of the "mixed potential," which postulates two or more separate reactions governed by a common electrode potential.

The fact that the dissolution of aluminum in alkaline solutions is probably governed by an electrochemical mechanism was first shown by Müller (3) and Straumanis (4) in their studies on the effect of impurities on the rate of dissolution. The more recent work by Streicher (5) gives further support to an electrochemical mechanism and treats the kinetics of the process in considerable detail. The experimental data presented in this study lend further support to the fact that the dissolution of aluminum in neutral and alkaline solutions is governed by an electrochemical mechanism.

Since the thermodynamically reversible potential of aluminum is about −1.6 v in neutral solutions and about −2.6 v in alkaline solutions while that of the ferrocyanide-ferricyanide system is about +0.25 v (6), it is evident that both reactions show a large polarization effect, so that the dissolution of aluminum is under both anodic and cathodic control.

The ferricyanide-ferrocyanide system is highly irreversible chemically as well as thermodynamically on aluminum, since the anodic reaction is predominately the dissolution of aluminum. In the *p*H range of about 3.0 to 10.0, the reduction of ferricyanide also approaches zero when a steady state is reached. Since the extent of this reaction, as indicated by the magnitude of $(I_c)_d$, decreases with time, it appears that a film, or barrier, forms on the aluminum surface which spreads out laterally. It is interesting to note that the *p*H range wherein this phenomena occurs is approximately coincident with that wherein aluminum hydroxide is stable (7).

The "real" anodic polarization curves indicate that the anodic reaction is a function of the *p*H. Polarization is very great below *p*H of 11.0, and decreases above this value. There is a considerable decrease at *p*H values of 13 and higher.

The "real" cathodic polarization function is also dependent upon the *p*H. As indicated above, in the range of 3.5 to about 10 it appears that only an extremely small portion of the surface is available to the cathodic reaction when a steady state is reached, while at *p*H values higher than 10.0 indications are that the whole of the apparent surface is functioning as a cathode. Caldwell and Albano (8) showed that the dissolution of aluminum in alkaline

solutions cannot be reduced appreciably or stopped by cathodic polarization; this was confirmed and shown to be dependent upon the fact that aluminum does not undergo any appreciable change in potential when made cathodic in these solutions (5).

The polarization curves shown in Fig. 10 and 11 give further confirmation as to why it is almost impossible to cathodically protect aluminum to any appreciable extent in strong alkaline solution. The hydrogen overvoltage curve levels off so rapidly that it is impractical to achieve the necessary negative potential.

A more detailed analysis and theoretical treatment on the behavior of aluminum with oxidation-reduction systems is planned for a future communication.

Acknowledgment

The author wishes to express his appreciation to Miss Anna A. Paolucci who performed the experimental work reported in this study.

Any discussion of this paper will be published in a Discussion Section, to be published in the June 1953 JOURNAL.

REFERENCES

1. J. V. PETROCELLI, *J. Electrochem. Soc.*, **97**, 10 (1950); **98**, 183 (1951).
2. O. GATTY AND E. C. R. SPOONER, "The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," p. 25, Oxford University Press, London (1938).
3. W. J. MÜLLER AND E. LOW, *Aluminium*, **20**, 257 (1938).
4. M. STRAUMANIS AND N. BARKASS, *Korrosion u. Metallschutz*, **15**, 5 (1939).
5. M. A. STREICHER, *J.* (*and Trans.*) *Electrochem. Soc.*, **93**, 285 (1948); **96**, 170 (1949).
6. W. M. LATIMER, "Oxidation Potentials," Prentice Hall, Inc., New York (1935).
7. M. J. N. POURBAIX, "Thermodynamics of Dilute Aqueous Solutions," p. 15, Edward Arnold & Company (London) (1949).
8. B. P. CALDWELL AND V. J. ALBANO, *Trans. Electrochem. Soc.*, **76**, 271 (1939).

Apparatus for Studying Electrogravitational Separations. Some Experiments on the Extraction of Sodium Chloride from Solution in a Flow System[1,2]

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ABSTRACT

As the first step in a systematic experimental investigation of an electrogravitational method for concentrating and separating simple electrolytes in solution, new and versatile apparatus has been constructed. The power supply is designed to furnish up to 50 amp to the experimental cell at potentials up to 0.7 v, controlled electromechanically to ±½ per cent. A Lucite cell with plane-parallel wire mesh electrodes has been adopted for flow experiments. Experiments on the extraction of sodium chloride were designed primarily to study electrode efficiencies in ranges of concentration and flow rate to which the method is applicable. Interesting qualitative comparisons with corresponding ion exchange experiments are developed.

INTRODUCTION

It has recently been demonstrated (1) that in certain electrolytic cells, especially designed to promote convection currents and operated below the decomposition potential of the solution, the combined effects of electrolysis, electromigration, and convection can be employed for the concentration and separation of electrolytes. The initial experiments pointed to a promising field of separative problems for exploration, and at the same time outlined the basic apparatus requirements and techniques.

The combined effects responsible for the separation have been termed "electrogravitational." This is actually a generic term for a number of electrochemical processes in which electrically initiated convection plays a decisive role in bringing about the desired end. For example, some well-known cells for the electrolysis of sodium chloride described in textbooks as "gravity cells" belong in this category. In the present instance, electrolysis of the solution itself is not involved, as explained below. The term "electrogravitational" is suggested by analogy with the thermal diffusion-convection separation process, which has been called the thermogravitational effect (2).

The principle involved in the method of (1) as exemplified by the apparatus described, is as follows: a solution of a chloride, MCl, is contained between two closely spaced vertical silver-silver chloride electrodes. On passage of direct current at low voltage (0.6 v or less), the following electrode reactions occur:

$$\text{cathode: } AgCl + e = Ag + Cl^-$$
$$\text{anode: } Ag + Cl^- = AgCl + e.$$

The combination of these electrode reactions with the migration processes leads to a horizontal concentration gradient, with MCl richer in the catholyte, and depleted in the anolyte. The density gradient thereby established leads to a convection current and the resultant concentration of MCl in the bottom of the cell. Two or more cations can be at least partially separated by virtue of their differences in cation mobility.

It should be emphasized that neither the quality nor quantity of electrolyte or solvent is changed during the process. By virtue of the low voltage employed, only the silver chloride is electrolyzed, and the reaction which occurs at one electrode occurs in exactly the reverse manner at the other. The net effect is the establishment of a concentration gradient in solution, which has a horizontal component due to electromigration and a vertical component due to convection.

Let us refer to the above type of cell with vertical electrodes a type V cell, and the corresponding cell with horizontal electrodes, the polarity of the upper

[1] Manuscript received August 6, 1951. This paper presented in part before the Division of Physical and Inorganic Chemistry at the 119th meeting of the American Chemical Society, Cleveland, Ohio, April 8 to 12 (1951). The authors have kindly consented to a delay in publication so that this paper may be included in the special Theoretical Electrochemistry Issue.

[2] Much of the experimental work is abstracted from the thesis of David Batzer, presented in partial fulfillment of the requirements for the degree of Bachelor of Science, 1951.

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and lower electrodes having been suitably chosen to eliminate convection, a type H cell. On passage of current, a stable vertical concentration gradient is also produced in the type H cell, but for practical separations, the type V cell is preferred for the following reasons: (*A*) The concentrated and dilute solutions are removed by convection to areas remote from the electrodes, where they can be removed as desired. (*B*) When the active electrode material AgCl is exhausted, it is necessary merely to reverse the electrical current in order to keep the process going. A new convection current is set up in the opposite direction, but electrolyte is still concentrated in the bottom of the cell. (*C*) With the type H cell, one obtains a concentration gradient determined solely by electromigration and electrode phenomena. This may be referred to as an elementary concentration process. In the type V cell, owing to the superimposed convection, a number of these elementary processes take place simultaneously in cascade; hence it is possible with a given applied potential to obtain greater degrees of concentration in the extremities of the apparatus than with the type H cell.

Some examples of the type H cell have recently been treated mathematically by Piguet, Kuhn, and Kuhn (3). Their very interesting results describe concentration and potential gradients as well as currents in the steady state. These authors have also commented on the multiplication effect to be expected in a type V cell when circulation of cathode and anode solution is "promoted." They report no experiments of this type, and the possibility of natural circulation provided by convection is not mentioned.

The present paper describes the first steps in a systematic experimental investigation of electrolyte separations based on the above considerations. The principal contribution is the construction of a versatile apparatus, which permits close control of the many variables. In (1), the current was reversed repeatedly on a program determined by the changing electrical characteristics of the cell; thus, the limited amount of active electrode material was used over and over again. The applied voltage varied during a half cycle. From the standpoint of interpretation of results, it is advantageous to operate the cell at constant voltage. A flow system has been constructed here in preference to the static system of the earlier work for two reasons. First, with regard to practical applications of the method, the superiority of the continuous flow over the batch process is generally recognized. Second, from a more academic point of view, the flow method permits a more readily observed correlation among the quantities: faradays consumed, equivalents removed, and amount of active electrode material used up. These two considerations apply primarily to the use of the method in concentrating electrolytes. There are further advantages of the flow method in separating two or more electrolytes, but this will not be discussed here, since no such separations are described in this paper.

In the first series of experiments with the new apparatus, the removal of sodium chloride as a solution passes between two Ag-AgCl electrodes maintained at constant potential is studied. The current is not reversed at all during an experiment, for it is desired to observe the characteristics of the cell under such conditions that all active electrode material is used up. We wish to (*a*) establish the general character of the effluent concentration curves, (*b*) determine the concentration factor and current efficiency at a number of concentrations and flow rates, and (*c*) provide a background of information which may be applied, for example, to selecting the proper frequencies for current reversal, when continuous concentrations or separations are desired.

When the cell is operated in the manner described, it should be recognized that the electrolyte removal is not entirely electrogravitational in action; part of the electrolyte is removed by straight electrolysis and electromigration, and becomes locked in the electrode framework. This type of study is a necessary preliminary to other methods of cell operation in which the net removal of electrolyte, after a sufficient number of current reversal cycles, will be entirely electrogravitational in nature.

Experimental

Power supply.—This item calls for the unusual requirement of heavy d-c currents at voltages of the order of only 0.5. It is also necessary that the voltage be constant during a run, and that it be adjustable in the range 0 to 0.7 v. Furthermore, although the experiments reported here never demanded more than 1.2 amp, a power supply capable of delivering up to 50 amp was desired for future work. A transformer-selenium rectifier combination with electromechanical voltage regulation seemed to be the only answer to these requirements. If a three-phase, full-wave bridge rectifier system is used, the a-c ripple is only 4 per cent at 360 cycles, a value which is not objectionable for the type of experiments contemplated; thus, the difficult filtering problems which are encountered at these high currents are avoided.

A power supply meeting these requirements is illustrated in block diagram in Fig. 1; it was constructed primarily from the purchased components listed in the legend. The reversing relays, pulse relay, and electric timer were included for experiments involving periodic current reversal; no ex-

periments of this type are reported here. The shunt bank contained manganin resistance units of 0.1, 0.02, 0.05, 0.01, 0.005, 0.001, and 0.0005 ohm. These resistances were selected so that the currents employed could be conveniently plotted on the 10 mv span of the recording potentiometer.

The motor control circuit was patterned after that of Glaser (4). Error signals from the voltage

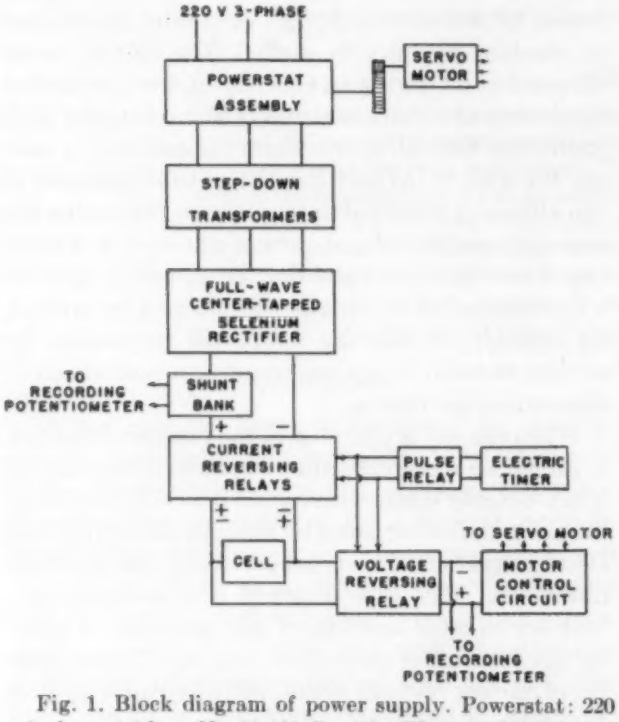

Fig. 1. Block diagram of power supply. Powerstat: 220 v 3-phase, 1.2 kva, No. 20-3Y, Superior Electric Co., Bristol, Conn. Three step-down transformers with 100:1 ratio and rectifier stack designed for an output of 50 amp furnished by the Electronic Rectifier Co., Rochester, N. Y. Current reversing relays: four SPST aircraft units (war surplus) with 12 v d-c coils and 50 amp contacts. Pulse relay: series 900, 110 v a-c coil, DPDT ¼-in. silver contacts, Advance Electric and Relay Co., Los Angeles, Calif. Electric timer: "Cycl Flex," hp 27, 250 min dial, Eagle Signal Corp., Moline, Ill. Voltage reversing relay: Series 200, DPDT, 12 v d-c coil, Guardian Electric Co., Chicago, Ill. Servo motor: No. 1282D with 300:1 gear box, Kollsman Instrument Div., Square D Co., Elmhurst, N. Y. Not shown: 12 v d-c power supply for operating relays. Other components, see text.

terminals of the cell are fed through a mirror galvanometer-phototube assembly to one of two thyratrons and an output transformer. The particular thyratron which happens to be firing in response to the signal determines the direction of rotation of the motor to correct the error, by adjustment of the powerstat. We have modified the circuit of Glaser by replacement of the two 929 phototubes by a single 920 dual cathode phototube, and by fitting the output transformer to the specific requirements of the motor. The galvanometer used for error detection was a Leeds and Northrup lamp and scale box type, Catalog No. 2420; it was part of a potentiometer circuit, and was heavily overdamped to eliminate "hunting."

The entire voltage controlled power supply assembly has given very satisfactory service. Control is within $\pm\frac{1}{2}$ per cent from zero to capacity current. Response time is the order of a few seconds, which is entirely adequate for our purposes.

During a run, both current and cell voltage were recorded continuously by a Brown multiple record potentiometer. One record consisted of the voltage from the proper shunt, and another record the voltage from the cell after dividing the latter with a volt box to match it to the recorder span.

Constant temperature chamber.—Cells were mounted in a constant temperature air bath controlled at 25 ± 0.2°C by a mercury thermoregulator-electronic relay system. Cells were mounted on a Julius suspension to minimize vibration. The three suspension wires were hung from a massive ceiling joist and passed through holes into the constant temperature chamber.

The cell.—Experience with a number of cell designs has determined the basic characteristics to be incorporated in the present cell.

1. The desirability of plane parallel electrode system over the concentric cylinder type had been clearly indicated in some experiments with the two cells of the latter design described in (1). This preference results from the fact that the performance during unidirectional current flow depends on which of the electrodes is cathode; a significant difference in a concentration-time curve is obtained when the electrode polarities are reversed. Identity of performance regardless of polarity should be expected, however, for the plane parallel electrode system.

2. Electrodes in some type of grid form, such as silver wire mesh supporting substantial amounts of silver chloride, are to be preferred to the smooth electrodes; in the latter case the number of faradays that can be passed in one direction before exhaustion of active electrode material is sharply limited.

3. Electrode spacings should be held as small as is consistent with freedom from fouling problems.

4. The cell should be capable of easy assembly and disassembly for inspection.

These suggestions were applied in the construction of Cell III (Fig. 2), which was designed for flow operation. Each electrode consisted of three layers of silver wire mesh, 30 mesh x 0.014-in. wire. The body of the cell was of Lucite in four parts, which could be screwed together, the joining faces being made leak-tight with stopcock grease. The rectangular channel formed after assembly was 1 x ¼ in.; however, the electrodes filled much of the gap, and

the minimum electrode separation was about $\frac{3}{32}$ in. The electrodes were 9 in. long. During a run, solution flows up through the cell and out the miniature conductance cell at the top.

The cell was put into operation initially by electrolytically chloridizing one electrode heavily with an applied potential of about 2.5 volts overnight. The electrolyte was 0.5*N* HCl, passed slowly through the cell. Hydrogen was evolved at the cathode. Later experiments showed that about 0.1 equivalent of silver had been converted to the chloride.

The pump.—A miniature glass reciprocating pump made from a 1 ml syringe and operated by a 110 v d-c geared motor was used to pump solution through the cell. The check valves were of Pyrex glass, hand ground into their seats until leakage was negligible. Variable motor speeds were obtained by feeding the armature winding from a variable d-c supply; the latter was a Varitran-transformer-selenium rectifier combination fed from the 110 v a-c line. Flow rates were constant to ±1 per cent.

Experimental Technique

The solutions were deoxygenated prior to an experiment by bubbling nitrogen through them for one-half hour, in order to avoid a side electrode reaction to be discussed later. They were then subjected to suction from an aspirator until degassing was complete; this was necessary because gas bubbles which form in the solution are detrimental to proper functioning of the pump valves. The solutions were analyzed and kept in tightly stoppered bottles until used.

A run was carried out in the following manner. First, any electrolyte absorbed in the electrode framework from a previous run was removed by repeated washings with distilled water. The water was allowed to stand in the cell for periods of several hours. During this procedure the electrodes were shorted out to insure that there would be no residual voltage when the next run was started. Then the cell was swept out for an hour with nitrogen. Starting with an empty cell, the flow of solution into the cell was begun, and a potential of 0.5 v applied. After the cell was filled, solution began issuing from the conductance cell into a graduated receiver. At the same time, a Leeds and Northrup conductance recorder was started. This instrument had three full scale ranges of 0–0.1, 0–0.01, and 0–0.001 reciprocal ohm. As time went on, readings were also taken of the volume of solution in the graduated receiver. During an experiment, the current was maintained unidirectionally until active electrode material was exhausted; for the next experiment, the current was simply reversed. No significant difference in performance was found due to the reversal of polarity.

Early experiments had given effluent solutions of abnormally high *p*H, up to 9.2, when starting with neutral solutions. It was concluded that the competing cathode reaction $\frac{1}{2}\,O_2 + H_2O + 2e = 2\,OH^-$ was responsible. After deoxygenating treatments on both solution and cell were adopted as a regular procedure, the effluent *p*H was normal.

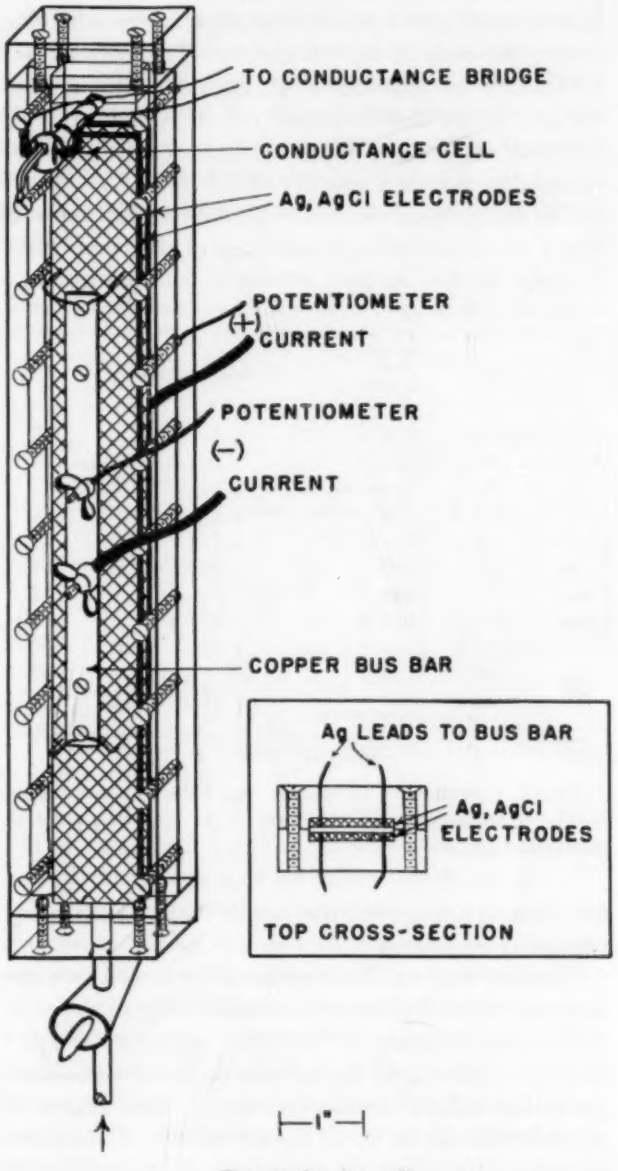

FIG. 2. Lucite cell

RESULTS

General character of the curves.—Fig. 3 shows a comparison of the effluent conductance in arbitrary units and current as a function of time in a typical run. The zero of time is taken at the point where solution begins issuing from the conductance cell; thus, in the case illustrated, nearly four hours were required to fill the cell.

The magnitude of the current is the result of two

competing resistances in the cell: the resistance of the electrolyte itself, and the continually increasing resistance due to depletion of active electrode material. (We do not consider the resistance of silver chloride films on the electrodes as of particular significance in the present experiments.) The current rises steadily while the cell is being filled. After a period of time the effective resistance due to depletion of electrode material becomes appreciable and lowers the rate of rise of current. The current will eventually go through a maximum, although not necessarily at the time the cell is just filled, and then fall as the depletion of electrode material assumes dominating importance.

The fluctuating character of the current curve of Fig. 3 was observed to some extent in all experiments. It may be due in part to slight nonuniformity in

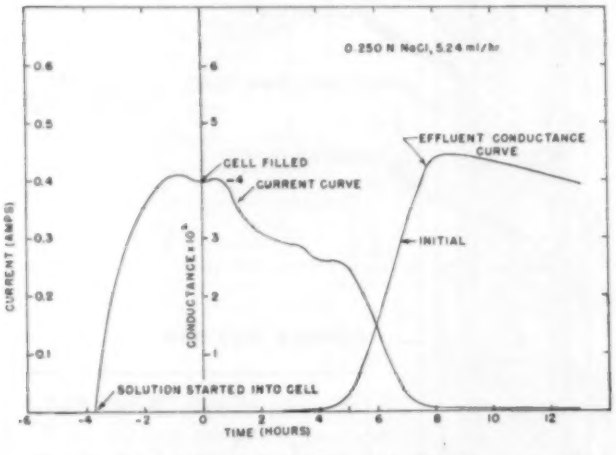

FIG. 3. Comparison of current and effluent conductance curves (Conductance in arbitrary units). Arrows refer to point A of text.

electrode spacing, but the major cause is probably turbulent convection.

Turning now to the conductance curve, we see that the original effluent is substantially depleted of electrolyte; a break in the curve begins at about 4 hours, the curve goes through a maximum well above the initial influent conductance, and then begins to approach the latter value asymptotically. It is interesting at this point to compare our type of curve with the corresponding ion exchange concentration-time "break-through" curve, which rises to the influent value without going through a maximum as the resin becomes saturated. In our case it should be remembered that electrolyte which is concentrated in the cell through action of the current is only temporarily retained. Concentrate that is locked in the electrode framework or has fallen to the bottom by convection eventually finds its way into the flowing solution. The effluent solution may, therefore, become more concentrated than the influent.

If a reservoir had been provided below the electrodes to collect the concentrate so that it could not mix with the influent, it would be expected that the effluent conductance curve would exhibit a much smaller maximum, or possibly none at all. Experiments of this type are planned, but have not yet been carried out.

Effect of flow rate and concentration.—For a given electrolyte concentration the lower flow rates would be expected to result in "cleaner" separations. As observed by reference to Fig. 4, this expectation is borne out in practice. In this figure the time scale has been multiplied by the concentration and flow rate; the units are thus equivalents of NaCl. While the total quantity of electrolyte removed up to the end of the break-through period is about the same in each case, the steepness of the break-through portion increases as the flow rate decreases.

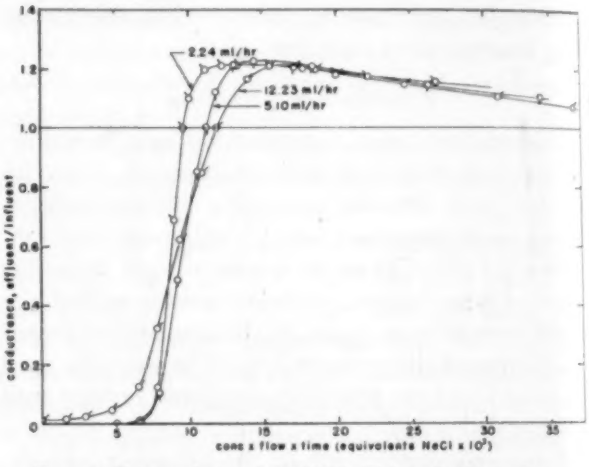

FIG. 4. Comparison of 0.5*N* NaCl break-through curves at different flow rates.

The horizontal ion transport velocity does not depend upon the flow rate, since it is maintained at the same value by the constant applied potential. It is the ratio of the linear flow velocity to the ion transport velocity that determines the slope of the effluent conductance vs. equivalents curve; as zero flow velocity is approached, the slope should approach infinity.

The effect of concentration on the character of the curves at comparable flow velocity is shown in Fig. 5. We employ as a reference point on the curves the influent conductance, designated as point A. A more gradual break is evident as the concentration decreases, and the maximum relative to point A becomes much more pronounced.

Significant quantities calculated for a number of curves are listed in Table I. A concentration factor α is defined as the ratio of the influent conductance to the initial effluent conductance, and the efficiency, η, is defined as the number of equivalents removed

per faraday[5]. The number of equivalents removed and the number of faradays up to point A were determined from the areas under the conductance and current curves respectively. A polar planimeter was employed for area measurements.

Before discussing the trends brought out in the table, we shall comment on the rather disappointing reproducibility. Separation factors are reproducible within ±10 per cent and efficiencies within ±5 per cent. The latter figure is reserved, however, for those experiments, in the large majority, where there was no suspicion of electrode fouling.

Difficulties due to electrode fouling and deterioration were almost completely absent and in any event were unlike those mentioned in (1). No suspended silver chloride was observed in the effluent

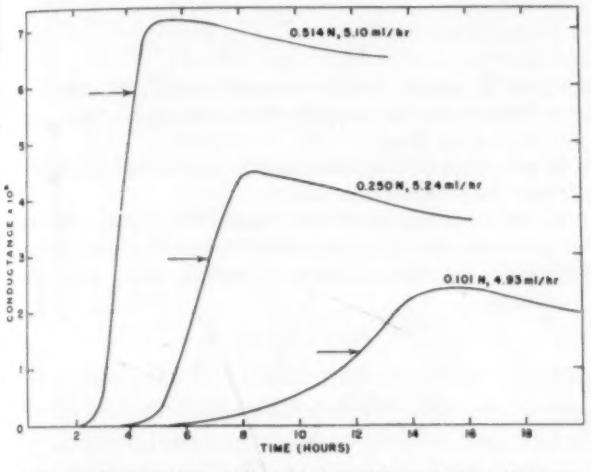

FIG. 5. Comparison of break-through curves at different concentrations. (Conductance in arbitrary units.)

except during the first run, when the electrodes had been freshly prepared. Results from runs 21 through 25 gave abnormally low efficiencies. This was traced to a minute solid bridge which had developed between the electrodes. After run 25 the cell was disassembled and the fault corrected. We are not able to say that the problem of electrode deterioration has been completely solved, but it appears likely that only a small increase in electrode spacing would provide freedom from fouling.

In order to show up any permanent electrode changes with time, the run number is also listed in Table I. There is evidence from the small but progressive increase in faradays with run number that the total amount of silver chloride increased in the cell over 30 runs by about 15 per cent. The small residual or diffusion current present in all runs, persisting after all active electrode material was used up and no further electrolyte removal occurred, may account for this factor. This residual current appears to be independent of electrolyte concentration, but is relatively more important for the low concentration runs, which involve smaller total currents. However, the efficiencies appear to be only slightly affected by it.

It was also observed that, in time, the pores of the top layer of silver mesh became almost completely filled in with the Ag-AgCl mixture. This could be expected to change the character of the separation process to some extent, and the number of faradays passed may be due as much to the accessibility of active electrode material as to its actual amount.

TABLE I. *Concentration factors and efficiencies for* NaCl

Run	Normality	Flow (ml/hr)	α	Equivalent removed	Faradays	η
26	0.5	4.3	280	0.0097	0.115	0.085
13	0.5	5.1	200	0.0093	0.126	0.074
7	0.5	12.5	72	0.0080	0.108	0.074
27	0.25	5.2	130	0.0077	0.113	0.068
22	0.26	7.1	46	0.0081	0.139*	0.058
14	0.26	15.5	33	0.0077	0.110	0.070
21	0.10	4.9	72	0.0048	0.119*	0.040
29	0.10	5.1	65	0.0058	0.124	0.046
30	0.05	5.2	43	0.0038	0.111	0.035
20	0.05	7.0	21	0.0037	0.099	0.037
8	0.05	13.0	15	0.0036	0.081	0.044

* These values are abnormally high due to partial short circuit in cell. See text.

The significant conclusions which can be derived from Table I may now be briefly summarized:

1. The concentration factor decreases sharply as the concentration decreases and as the flow rate increases. This is in accordance with expectation.

2. The concentration factor of 280 in the present work is a distinct improvement over the value of 100 reported for 0.5*N* NaCl in (1). The widely different techniques do not, however, make the figures strictly comparable. Furthermore, if we could determine a separation factor defined by the ratio of the highest concentration in the cell to the concentration of the initial effluent, all values in the table would be raised significantly.

3. The efficiency decreases by about ½ for a 10-fold decrease in concentration. Values given are reasonable in comparison with those obtained in (1), if the difference in technique is recognized.

4. The number of faradays passed to point A is about the same for all experiments. The slightly smaller value for 0.05*N* solutions is compensated by an increased amount beyond point A.

[5] The efficiency was originally defined in this manner in (1). It should be noted, however, that the ultimate theoretical efficiency obtainable for single electrolytes is numerically equal to the cation transference number, instead of to unity, as stated on p. 412 of that paper.

Applicability of the Method to Continuous Deionization

The above studies evidently form a basis for the design of a process for the continuous removal of electrolyte. To de-salt water continuously, for example, solution might be fed into a cell similar to that of Fig. 2 at some point above the bottom of the electrodes. Separation of electrolyte is accomplished by passage of current, reversed repeatedly at a definite frequency. The water, stripped substantially of electrolyte, would be withdrawn from the top, and concentrate from the bottom, each at a constant rate. When operated in this manner, the net removal of electrolyte is entirely electrogravitational in nature.

In further analogy of the method to ion exchange, the electrodes correspond to two ion exchange systems, with one electrode extracting electrolyte while the other is being regenerated. When the first electrode is spent, reversing the current simply reverses the functions of the two systems. Thus, what is essentially a batch process is converted into a continuous one, and in an extraordinarily simple manner.

The major field of applicability of the method will probably be with concentrated solutions where ion exchange is relatively inefficient.

Acknowledgments

One of us (GWM) gratefully acknowledges support from the Du Pont Grant-in-Aid made to the Chemistry Department of the University of Wisconsin, which made possible the construction of the power supply and voltage regulating unit.

We are indebted to the Research Committee of the University of Wisconsin for purchase of the recording conductance bridge with funds supplied by the Wisconsin Alumni Research Foundation.

Professor Paul Bender has given us much helpful advice in the construction of the voltage regulator. Mr. T. R. Lloyd of the Departmental Machine Shop machined the Lucite for our cell.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. G. W. MURPHY, *J. Electrochem. Soc.*, **97**, 405 (1950).
2. J. PIGUET, W. KUHN, AND H. KUHN, *Helv. Chim. Acta*, **34**, 1183 (1951).
3. S. R. DE GROOT, "L'Effet Soret," North Holland Publishing Co., Amsterdam (1945).
4. E. M. GLASER, *Electronic Inds.*, 104 (1944); See also BATCHER AND MOULIC, "The Electronic Control Handbook," p. 307, Caldwell-Clements, Inc., New York (1946).

Electrical Conductivity of Molten Cryolite and Potassium, Sodium, and Lithium Chlorides[1]

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ABSTRACT

An improved technique has been developed for the determination of the electrical conductivity of reactive molten salts and has been applied to cryolite. The method employs a platinum cell with two concentric hemispherical electrodes. This cell is maintained a fixed distance below the surface of the molten salt which is held in a larger platinum container. Errors from lead resistance have been eliminated by measuring with a Kelvin double bridge (Thomson bridge) and polarization difficulties have been minimized by extrapolation of the nearly linear plot of resistance vs. frequency$^{-1/2}$ to infinite frequency. Conductivities of molten potassium chloride, sodium chloride, and lithium cloride were determined with a quartz dip-cell. Best values for the conductivities (ohm^{-1}cm^{-1}) at 1000°C were: cryolite 2.80; potassium chloride 2.65_2; sodium chloride 4.17_4; and lithium chloride at 700°C, 6.14. Densities (g/ml), measured by a platinum sinker, were found to follow these equations from the melting points to 1080°C: potassium chloride $1.964–0.574 \cdot 10^{-3}t$; sodium chloride $1.969–0.524 \cdot 10^{-3}t$; cryolite $3.032–0.937 \cdot 10^{-3}t$. The logarithm of equivalent conductance (Λ) changed linearly with reciprocal absolute temperature (T). Best values for the activation energy for conductance (kcal/mole) (calculated as 2.303 times 1.986 cal/mole deg times slope of log Λ vs. $1/T$) were: cryolite 4.48; potassium chloride 3.32; sodium chloride 3.04; lithium chloride 1.70. Maintaining the fused cryolite in contact with an atmosphere of argon as compared with room air had a negligible effect upon the measured conductivity values for cryolite.

INTRODUCTION

The discovery by Charles Martin Hall in 1886 that molten cryolite would dissolve alumina in substantial quantities and that the solution was a good electrical conductor laid the foundation for the large-scale production of aluminum by the electrolytic process. Both the tremendous expansion of the industry and the decades of research since Hall's original discovery have emphasized the dominant position of cryolite in this electrolytic process. Anticipated production of aluminum in the United States in 1952 will require about 18 billion kwhr and at least one quarter of this power will be expended in overcoming resistance losses in the cryolite bath. A knowledge of the factors influencing the conductivity of cryolite with the additives that make up the Hall bath is thus highly desirable.

The object of this work was to determine the conductivity of cryolite with the highest possible accuracy. Measurements of this value are not lacking, but precision in the published work has been low because of the difficult problem of designing a conductivity cell for use with molten fluorides.

PREVIOUS MEASUREMENTS

In 1920, the two senior authors measured the conductivity of molten cryolite, employing a partially filled platinum cell with hemispherical electrodes similar in some respects to that of Jaeger and Kapma (1). In these measurements, Edwards and Taylor used a Kelvin bridge and in this way eliminated the resistance of the current leads in the calculation of conductivity. Measurements were made with 1000-cycle sine wave current and with an electronic amplifier in the detection unit.

The depth of electrolyte in the platinum cell was calculated from the measured weight and density of the fused salt and the dimensions of the cell. Difficulties from polarization were minimized by applying a fresh coating of platinum black to the electrode surfaces before each measurement. In spite of this precaution, there was a slow, measurable drift in the resistance of the cell when filled with molten cryolite. It is interesting that these early unpublished measurements check the present work so closely; the values of specific conductivity increased linearly from 2.73 ohm^{-1}cm^{-1} at 1000°C to 2.91 ohm^{-1}cm^{-1} at 1080°C.

The platinum cell used in 1920 was employed with some modifications for the measurements reported in this paper.

The first published electrical conductivities of any real value for cryolite were those of Arndt and Kalass (2). These workers employed a similar plat-

[1] Manuscript received March 24, 1952. This paper prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

inum cell and determined the height of electrolyte by observing the solidification pattern on a platinum probe. The resistance of the current-carrying leads was a major source of inaccuracy in their work; in one case the total resistance was 0.302 ohm of which the lead resistance was 0.186 ohm, leaving 0.116 ohm for the resistance of the salt. They recognized that their electrode areas were too small to eliminate polarization and these errors undoubtedly account in part for their low values of conductivity, that at 1000°C being 2.23 $ohm^{-1}cm^{-1}$.

Two measurements of cryolite conductivity appeared in 1936. Batashev (3) used a platinum cell shaped like that of Arndt and Kalass (2) but filled by immersion in a larger platinum crucible containing the electrolyte under investigation. With a high, but unspecified, frequency the specific conductivity for cryolite measured by a Wheatstone bridge was 3.23 $ohm^{-1}cm^{-1}$ at 1000°C. Cuthbertson and Waddington (4) avoided the low resistance of the platinum cell by using a magnesia tube with a long cryolite path between the electrodes. They must have experienced some solubility of magnesia in the cryolite; the average of their values at each measured temperature was low and reproducibility was poor. (The two values at 1020°C were 2.43 $ohm^{-1}cm^{-1}$ and 2.77 $ohm^{-1}cm^{-1}$.)

In a recent review article, Frejacques (5) listed the conductivity of cryolite as 2.80 $ohm^{-1}cm^{-1}$ at 1000°C but did not give data to substantiate this choice. Vayna (6) has measured the conductivity of cryolite, but his technique was that of Arndt and Kalass (2) and his values were also low (2.36 $ohm^{-1}cm^{-1}$ at 1000°C).

Several authors [Mashovetz (7), Mashovetz and Lundina (8), Batashev (9), Agnini (10), Bonnier and Andrieux (11)] have pointed out that cryolite loses fluorine values during exposure to room air at high temperature. Fischer (12) has found that for natural cryolite containing about 0.2 per cent water, the melting loss was 0.4 per cent, and for cryolite with 2.6 per cent water, the melting loss was 4.3 per cent at 1000°C.

Materials

Hand-picked crystals of pure Greenland cryolite were crushed to 20 mesh and any associated particles of galena were removed. This material was ignited for one hour in a platinum crucible at 600°C before each run, the weight loss being about 0.11 per cent. When the crushed cryolite was exposed to saturated water vapor for one month, 0.35 per cent water was adsorbed, but after two weeks' exposure to the laboratory atmosphere, the original weight was regained within 0.01 per cent.

Analysis of the cryolite ignited at 600°C compared with the theoretical values as shown in table below:

	F	Na	Al	K	Li
Analysis	54.34	32.76	13.01	.04	.007
Theory	54.30	32.86	12.84		

Spectrographic analysis showed only potassium and lithium as impurities at 0.1 to 0.01 per cent. Fluorine was determined by a Willard and Winter distillation over perchloric acid. Sodium was precipitated as sodium uranyl zinc acetate after decomposition with sulfuric acid. Aluminum was determined gravimetrically by ammonia precipitation after decomposition with sulfuric acid. Potassium and lithium were determined by the flame photometer. The agreement between actual and theoretical values is within the precision of the methods.

The potassium chloride was Bakers C.P. Analyzed; sodium chloride and lithium chloride were Eimer and Amend C.P. The salts were ignited before use for one hour at temperatures just below their sintering points.

Densities

Both the calculation of height of the molten salt in the partially filled conductivity cell from the initial weight of salt and the calculation of equivalent conductivity require an accurate knowledge of salt density as a function of temperature. Densities were determined with a hollow platinum sinker (calibrated from the room temperature density and the coefficient of expansion of platinum) suspended from an analytical balance by a fine platinum wire. The adherence of gas bubbles to the sinker was avoided by an initial immersion and rapid withdrawal. On reimmersion the frozen salt coating split off and detached any bubbles.

TABLE I. *Densities of molten cryolite, potassium, and sodium chlorides*

Material	Range of measurement °C	Density g/cm³	99% confidence limit (13)
Cryolite (14)	1000–1080	$3.032-0.937\cdot10^{-3}t$	—
Potassium chloride	800–1040	$1.964-0.574\cdot10^{-3}t$	±0.002
Sodium chloride	830–1100	$1.969-0.524\cdot10^{-3}t$	±0.002
Lithium chloride (15)	626–985	$1.762-0.432\cdot10^{-3}t$	

Densities were observed to change linearly with temperature according to the equations of Table I for the materials measured in this work.

Furnace and Temperature Measurements

The furnace was of the crucible type (chamber 4 in. in diameter by 6 in. deep) with a nichrome

resistor; the power input was regulated by a Variac transformer. A Leeds and Northrup type K-2 potentiometer in combination with a platinum-platinum rhodium thermocouple (protected in some cases by a platinum sheath) with the junction inside the inner electrode gave temperatures precise to 0.1°C. The thermocouple was calibrated at the freezing point of low-alkali sodium fluoride 993°C. The cell temperature was held within a degree for the several minutes required to make the conductivity measurements.

Electrical Components

The bridge current was supplied by a Hewlett-Packard signal generator model 205A having a frequency range of 20 to 20,000 cycles/sec and a variable output up to 5 watts. The resistances for the bridges were noninductive, shielded units accurate within 0.2 per cent. They included a decade bridge and 50-ohm and 0.1-ohm standard resistances. A four-stage amplifier was employed in the detector circuit. The capacitors were high quality shielded, air or mica insulated units. Earphones, a vacuum tube voltmeter, and an oscilloscope have been used to measure null points in the bridges.

The connections were made with shielded wire. Fixed noninductive resistors of about 25 ohms were inserted in each side of the oscillator output when it was used with the Kelvin bridge. The usual signal strength impressed on the circuit was 10 volts, which with the resistance of about 50 ohms led to currents near 0.2 amp in the principal circuit. A Kay-Lab model 503A, bridged T-type filter between the first and second stages of the amplifier reduced 60 cycle interference to a low level.

The Kelvin bridge circuit is diagrammed in Fig. 1. The variably coupled inductance (shielded and of negligible resistance) was suggested by Wenner (16) to compensate for the capacitance in the cell. To control the frequency dependence of the circuit, a variable capacitance, Cg, was connected from ground to the input side of the bridge. To determine the bridge frequency dependence, noninductive resistances of the values to be measured were soldered across the leads just above the Lavite block. Assuming that the reading at a low frequency was the true resistance, deviations at higher frequencies were applied as corrections to the readings with the cell. The two variable resistances of the Kelvin bridge circuit were always kept at equal settings.

Polarization

Jones and Christian (17) have verified the Warburg law that the polarization resistance of a cell is inversely proportional to the square root of frequency (f) in the audio range. They suggested that resistance be measured at a series of frequencies and extrapolated to infinite frequency where the polarization resistance would be zero. In this work, resistances measured at 500, 1000, 2000, and 4000 cycles/sec were plotted against $1/\sqrt{f}$ and the linear extrapolations to infinite frequency were used in calculation.

Polarization is particularly bad in the platinum cell because the resistance is only 0.1 to 1 per cent of that usually recommended and because the usual layer of depolarizing platinum black loses efficiency at high temperatures. Polarization is much less important in high resistance dip-cells, and these have been used to establish the conductivities of chlorides. It was hoped that these salts could subsequently be employed to standardize the platinum cell.

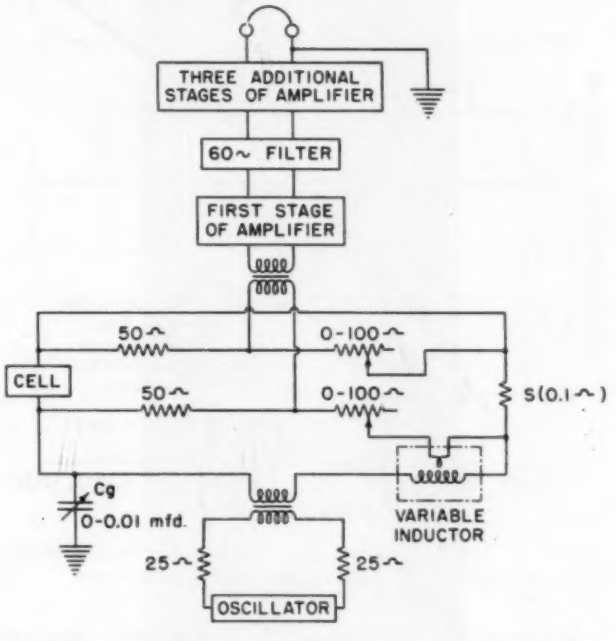

Fig. 1. Bridge circuit

Dip-cell Determination of Conductivities

The first purpose of this phase of the work was to establish the conductivities of potassium, sodium, and lithium chlorides as possible standards for the platinum cell. A few direct values for cryolite were also attempted in dip-cells, but these were unreliable because of the high reactivity of cryolite.

Cell Construction and Circuit

The cell was simply constructed of two 3-cm pieces of 1-mm I.D. quartz capillary, each sealed to a piece of 8-mm quartz tubing. The two tubes and a platinum-sheathed thermocouple were held between two pieces of Transite bolted to a clamp. Platinum electrodes were bent into cylindrical form and welded to platinum lead wires of large diameter. A Wheatstone bridge was used with the usual variable capacitor for

balancing cell capacitance. Suitable corrections were made for the relatively small lead resistances.

Experimental Procedure

The cell constant was determined with a 31.1 per cent sulfuric acid solution (resistivity 1.213 ohm cm at 25°C) (18) contained in a platinum crucible. The cell showed no appreciable change after use with fused chlorides. When the electrodes were well platinized, the measured resistance of the standard sulfuric acid was nearly independent of frequency. The cell constant was about 500 cm^{-1} and thermal expansion was calculated to cause the negligible decrease of 0.04 per cent over an 800°C range.

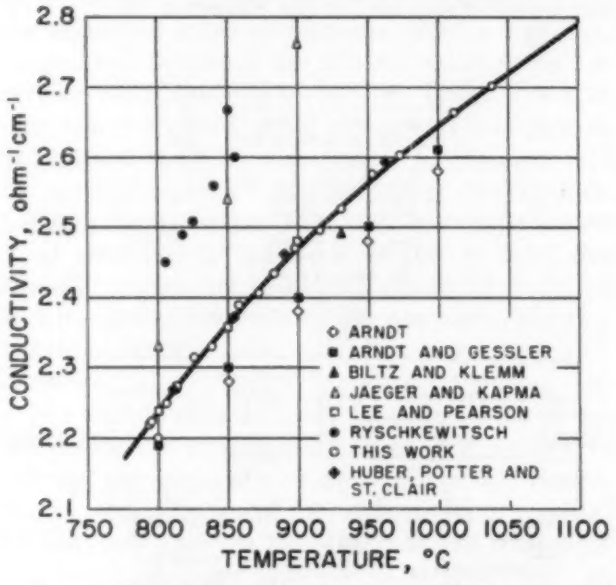

FIG. 2. Electrical conductivity of molten potassium chloride. [Arndt (19); Arndt and Gessler (20)].

No appreciable change in cell resistance resulted from movements of the dip-cell inside the sulfuric acid in the platinum crucible, provided that the lower ends of the capillaries were at least 1 cm above the bottom of the crucible and provided that the platinum electrodes were immersed in the liquid to a depth of at least 3 mm. Vertical movements of the electrodes within the tubes changed the cell resistance markedly and the electrodes had to be seated solidly on the shoulder between the capillary and 8-mm tube.

Results

The results of two determinations of the conductivity of molten potassium chloride plotted as a function of temperature are shown in Fig. 2 in comparison with values in the literature. The agreement with the data of Lee and Pearson (21) and of Huber, Potter, and St. Clair (22) is excellent. The conductivity of the molten potassium chloride did not change during three hours heating at 940°C. Conductivity values at 50°C temperature intervals from the smoothed curve from 800 to 1050°C are listed in Table II.

The conductivity values for sodium chloride from six determinations are plotted against temperature along with the literature values in Fig. 3 and agree most closely with those of Lee and Pearson (21)

TABLE II. *Best values for the electrical conductivities of molten potassium and sodium chlorides*

Temp °C	Conductivity, $ohm^{-1}cm^{-1}$	
	KCl	NaCl
800	2.24_8	3.58_2
850	2.36_1	3.75_4
900	2.46_7	3.90_6
950	2.56_4	4.05_0
1000	2.65_2	4.17_4
1050	2.72_8	4.29_2
1100	2.79_6	4.39_2

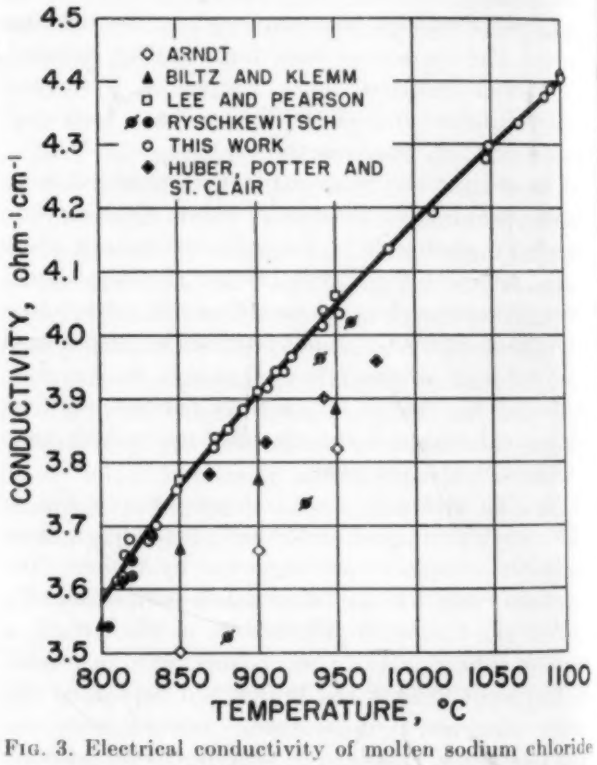

FIG. 3. Electrical conductivity of molten sodium chloride

with, however, a greater departure from linearity. Best values at 50°C temperature intervals from 800° to 1100°C are listed in Table II.

An attempt to measure the conductivity of lithium chloride with a quartz cell in air was only partially successful. After points at 619°, 664°, and 698°C where the conductivity was 5.80, 5.99, and 6.13 $ohm^{-1}cm^{-1}$, the cell resistance decreased at irregular intervals, apparently as the quartz tubes cracked. The first three points are in good agreement with Biltz and Klemm (23) who used a quartz U-tube cell

under an atmosphere of carbon dioxide and observed only slight attack on this cell by the melt. The data of Ryshkewitch (24) for lithium chloride are apparently in error. The quartz tubes changed very little in shape during the run, but the originally amorphous quartz was transformed to small needle-like crystals of alpha quartz, all perpendicular to the axis of the tube. The final melt of lithium chloride was quite alkaline, a sign of considerable hydrolysis during the measurement. The density of lithium chloride was taken (15) from the expression: $d_w^t = 1.762 - 0.432 \cdot 10^{-3}t$.

In two attempts to determine the conductivity of cryolite with a quartz cell, the quartz was attacked before precise values could be taken. The greatest attack was at the surface of the melt and the inside diameter of the capillary was not noticeably changed. Approximate values of conductivity of cryolite before the tubes broke were 3.11 $ohm^{-1}cm^{-1}$ at 1070°C and 500 cycles/sec, and 2.83 $ohm^{-1}cm^{-1}$ at 1019°C and 1000 cycles/sec.

Partially Filled Platinum Cell

The platinum cell used in this work was of 50-ml volume and had cylindrical sides and hemispherical bottoms supported by four platinum rods on the outer electrode and two on the inner. These rods also served to connect the cell electrodes to the Kelvin bridge. The rods were rigidly fixed in two blocks of baked Lavite, which kept the electrodes in the same relative positions, and also supported the cell in the furnace. The Lavite blocks were held together with steel bolts plated with platinum. The cell is shown in Fig. 4.

Cell Constants

The cell constant determined by the Kelvin bridge with the 31.1 per cent solution of sulfuric acid at 25°C for a volume of 50 ml was 0.1122 cm^{-1} with a standard deviation of 0.00086 cm^{-1} (cell resistance approximately 0.1 ohm). With the same volume of 0.01*N* aqueous potassium chloride solution measured with a Wheatstone bridge (cell resistance approximately 80 ohms) the cell constant was 0.1121 cm^{-1} with a standard deviation of 0.00073 cm^{-1}. It is gratifying to have this direct check on the Kelvin bridge and the methods for cell capacitance compensation.

The Kelvin bridge circuit was used at high temperatures. The cell constants at various temperatures and volumes were checked periodically by measuring the resistance of the cell filled to the desired volume with molten potassium chloride. Cell standardizations with sodium chloride were not accurate for reasons which have not been established. This subject is discussed in a later section.

Results

Resistance readings were corrected for the frequency dependence of the bridge and extrapolated to infinite frequency and zero elapsed time after melting. The time correction was equivalent to about 1 per cent per hour of heating. Even this correction was subject to considerable error in that no allowance was made for volatilization during melting.

Fig. 4. Conductivity cell

The best values for the electrical conductivity of cryolite from these determinations were 2.82 $ohm^{-1}cm^{-1}$ at 1000°C, 2.91 $ohm^{-1}cm^{-1}$ at 1040°C, and 2.99 $ohm^{-1}cm^{-1}$ at 1080°C.

Volatilization and Reaction with the Atmosphere

To establish the reason for time effects observed with the partially filled platinum cell, a platinum crucible containing molten cryolite was suspended in the furnace by a platinum wire from an analytical balance and weight loss was measured as a function of time and temperature in various atmospheres. The weight loss was adequate to explain the observed increase in resistance of the molten cryolite in the platinum cell. The rate of weight change was not greater for air than for argon nor for wet air than for dry air.

Immersed Platinum Cell Determination of Conductivities

The partially filled platinum cell for measuring conductivity of complex systems is subject to the following principal disadvantages:

1. Inaccuracies in time extrapolation.
2. Difficulty of securing good mixing of multicomponent salt systems prior to the conductivity determinations.
3. Dependence on accurate density determinations.
4. Sensitivity of the relatively small volume of melt to accidental impurities picked up during the heating.
5. Possible thermal discontinuities in the melt.
6. High dependence of cell constant on temperature.

In each of these respects, complete immersion of the cell in a platinum crucible containing the stirred molten salt with frequent adjustment to a fixed depth below the surface offered substantial advantages.

Cell Arrangement

A 400-ml platinum crucible 9.5 cm deep and 7 cm in diameter was used for the bath of molten salt in which the conductivity cell was immersed. The cell was suspended by a rod which rested on the upper end of a fine screw control with a vernier scale. A platinum wire to serve as a feeler point was welded to a rigid platinum rod which was securely fastened to one of the spacers between the Lavite blocks. An electrical circuit through a resistance meter from this platinum feeler to one of the cell electrodes determined feeler contact with the liquid. There was a difference of about 0.6 mm between the points of making and of breaking contact; the point of making contact which was reproducible within 0.03 mm was employed. The feeler was set 1.6 mm above the top of the cell so that the cell would always be completely submerged even though it might not be perfectly aligned in every run. The reproducibility in cell depth corresponded to a range of only 0.15 per cent in cell constant. The lateral position of the cell within the platinum beaker was without measurable effect as long as the cell was maintained several millimeters from the walls.

An unsheathed thermocouple was led to the bottom of the inner cup of the cell through a porcelain tube held rigidly in the center holes of the Lavite blocks.

Cell Constants

It was known from the earlier work that platinum black was converted rapidly in these fused salts to platinum gray, which is partially effective in reducing polarization. In an attempt to achieve maximum reproducibility, the cell was platinized initially and was not replatinized throughout the subsequent determinations. Actually the platinum gray continually lost its depolarizing ability, and in the later runs the lowest frequency at which the bridge could be balanced had to be taken as 600 cycles/sec.

The constant of the well-platinized cell at room temperature as measured with 31.1 per cent sulfuric acid was 0.0840 cm^{-1}. The resistance changed linearly with frequency$^{-1/2}$ from 500 to 4000 cycles/sec and decreased only 3 per cent between 500 cycles/sec and infinite frequency. After a sodium chloride run, the change became about 25 per cent, and while the points no longer fit exactly on the linear plot, the cell constant did not change more than 1 per cent, nor did it in subsequent determinations. The change in resistance with frequency increased irregularly to 30 per cent between 500 cycles/sec and infinite frequency as the runs continued. After the series of runs was completed, the cell was replatinized and its constant redetermined as 0.0847 cm^{-1}.

The cell constant would be expected to decrease on heating approximately linearly with the expansion of the platinum, and at 1000°C the expansion of 1.0 per cent would lead to a cell constant of about 0.0835 cm^{-1}.

Attempts to determine the cell constant directly at high temperatures by the use of sodium chloride led to anomalous results. The values of resistance decreased about 25 per cent from 500 cycles/sec to infinite frequency and plots of resistance vs. frequency$^{-1/2}$ were not exactly linear. The curvature was such that higher resistances (and hence higher cell constants) resulted from extrapolation of the 2000 and 4000 cycle/sec resistances than from the 500 and 1000 cycle/sec resistances. Extrapolation of the 2000 and 4000 cycle/sec resistances gave the expected values just above the melting point (808°C), but these frequencies at temperatures above 1000°C led to a cell constant about 5 per cent too high. The apparent effect then for any given frequency extrapolation was that cell constant increased quite rapidly with temperature. This erroneous result probably implies that resistance has not been measured at high enough frequencies for accurate extrapolation to infinite frequency with sodium chloride.

The cell constant determined with molten potassium chloride is much more consistent than with sodium chloride. Resistance changes less rapidly and more linearly with frequency$^{-1/2}$. The apparent cell constant increased only from 0.0836 cm^{-1} at 851°C to 0.0854 cm^{-1} at 1086°C in the first run. In successive determinations the apparent cell constant in the 1000°C range decreased to 0.080 cm^{-1}.

In view of this unsatisfactory behavior with the molten chlorides, it has seemed best to use a cell constant of 0.0835 cm^{-1} independent of temperature, as calculated from the room temperature value (which was constant throughout this work) and the coefficient of expansion of platinum.

Results

The results of runs with cryolite are shown in Fig. 5 and the calculation for a typical point (from the fifth run) is outlined in Table III. The values were essentially independent of whether the temperature was increasing or decreasing before the point was taken. The first two cryolite runs were made before the final sequence was started and the third represents the first run of the final sequence.

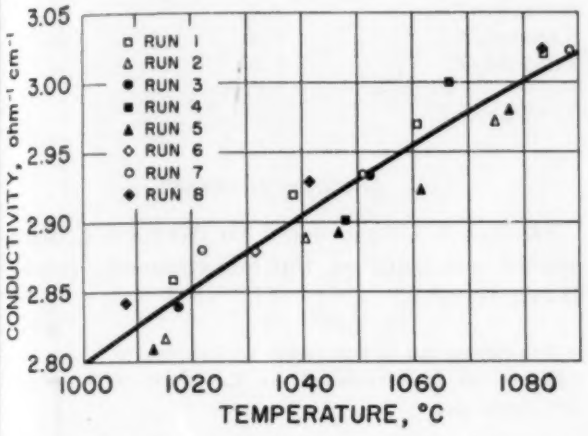

FIG. 5. Electrical conductivity of molten cryolite measured by the immersed cell method.

TABLE III. *Typical data for calculating cryolite conductivity*

Temp °C	Frequency cycles/sec	Cell resistance			Cell constant cm^{-1}	Conductivity $ohm^{-1}cm^{-1}$
		Measured ohms	Corrected ohms	Infinite frequency ohms		
1045.4	4000	0.03018	0.03007	0.02888	0.0835	2.89
—	2000	0.03060	0.03053			
—	1000	0.03132	0.03130			
—	500	0.03211	0.03211			
1047.3	4000	0.03014	0.03004			

The plots of resistance vs. frequency$^{-1/2}$ for the first cryolite runs were quite linear and the decrease from 500 cycles/sec to infinite frequency was about 10 per cent. In subsequent runs the slope of the frequency plot increased, although in many cases the linearity was maintained. Values of apparent conductivity increased for the later runs and these results have not been plotted. The best values of conductivity by this method are 2.80 $ohm^{-1}cm^{-1}$ at 1000°C, 2.90 $ohm^{-1}cm^{-1}$ at 1040°C, and 3.00 $ohm^{-1}cm^{-1}$ at 1080°C.

Summary of Cryolite Conductivities

Three procedures have been employed with reasonable agreement in a determination of the electrical conductivity of molten cryolite. The quartz dip-cell cracked in cryolite, but the lowest initial value seems reasonably accurate. This affords a satisfying check on the other two methods because the sources of error should be different from those with the platinum cell. The partially filled platinum cell in which the salt height is determined by density measurements has given quite accurate values for conductivity. However, this cell is subject to errors from volatilization and creepage. The immersion of the platinum cell to a fixed depth in a larger platinum vessel filled with molten salt provides the simplest arrangement for measurement of cryolite conductivity. The necessity for precise knowledge of densities is eliminated and the effects of volatilization are minimized. Errors from lead resistance are removed by the use of a Kelvin bridge circuit and the attendant large polarization errors are minimized by extrapolating cell resistances to infinite frequency. The method is now sufficiently free of other errors that the inability to extrapolate resistance to infinite frequency is emphasized. This leads to an uncertainty of several per cent in the absolute conductivity of cryolite.

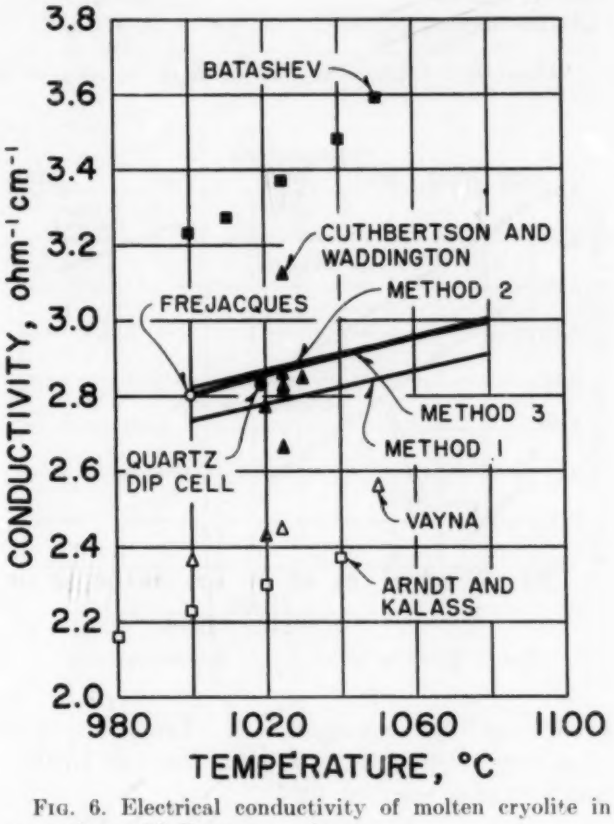

FIG. 6. Electrical conductivity of molten cryolite in comparison with literature values.

In Fig. 6 our values obtained by the several procedures employing the platinum cell (method 1, original work of Edwards and Taylor; method 2, partially filled cell; method 3, immersed cell) and the quartz dip-cell are compared with those in the literature. The agreement among these runs, although marred by experimental difficulties, is nevertheless

the most satisfactory which has been reported for fused fluoride conductivities. In our opinion the best values of the cryolite conductivity are those measured with the immersed cell. These are 2.80 ohm^{-1}cm^{-1} at 1000°C, 2.90 ohm^{-1}cm^{-1} at 1040°C, and 3.00 ohm^{-1}cm^{-1} at 1080°C.

for the chlorides decreases from potassium to sodium and more sharply to lithium and is higher for cryolite than for these chlorides.

TABLE IV. *Change of conductance with temperature*

Material	Log Λ	Log K	Activation energy for ionic migration (kcal) 2.303 × 1.986 × slope of log Λ vs. 1/T	
			This work	Bloom and Heymann (25)
Cryolite[a]	2.744–980/T	0.994–698/T	4.48	—
Potassium chloride	2.7235–726.64/T	0.810–492/T	3.32	3.26
Sodium chloride	2.7498–664.18/T	0.966–440/T	3.04	2.70
Lithium chloride	2.633–371.5/T	1.185–381/T	1.70	1.72

[a] Equivalent weight of cryolite taken as one third the molecular weight.

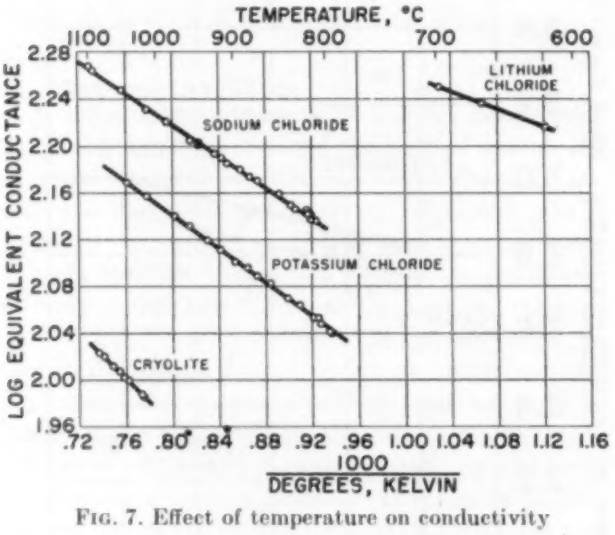
TEMPERATURE, °C
1100 1000 900 800 700 600
LOG EQUIVALENT CONDUCTANCE
2.28 2.24 2.20 2.16 2.12 2.08 2.04 2.00 1.96
LITHIUM CHLORIDE
SODIUM CHLORIDE
POTASSIUM CHLORIDE
CRYOLITE
.72 .76 .80 .84 .88 .92 .96 1.00 1.04 1.08 1.12 1.16
1000/DEGREES, KELVIN

FIG. 7. Effect of temperature on conductivity

EFFECT OF TEMPERATURE ON CONDUCTIVITY

All of the conductivity data can be plotted linearly as logarithm of equivalent conductance (Λ) against reciprocal absolute temperature (T) where $\Lambda = KE/d$, with K the specific conductivity, E the equivalent weight, and d the density (25, 26). Plots of the data for potassium chloride, sodium chloride, lithium chloride, and cryolite are shown in Fig. 7. The equations for these relations are listed in Table IV. Reasonably straight lines which are useful in calculations also result for log K vs. $1/T$ over a short temperature range and the equations for these lines are also listed. Values of the activation energy for ionic migration in kcal/mole calculated as 2.303 × 1.986 × 10^{-3} × slope of the plot of log Λ vs. $1/T$ are also listed and compared with the values of Bloom and Heymann (25). The "activation energy"

ACKNOWLEDGMENT

Dr. Lee A. Cosgrove and Mr. Kenneth E. Martin carried out many of the measurements discussed in this report.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. F. M. JAEGER AND B. KAPMA, *Z. anorg. Chem.*, **113**, 27 (1920).
2. K. ARNDT AND W. KALASS, *Z. Elektrochem.*, **30**, 12 (1924).
3. K. P. BATASHEV, *Legkie Metal.*, **10**, 48 (1936).
4. J. W. CUTHBERTSON AND J. WADDINGTON, *Trans. Faraday Soc.*, **32**, 745 (1936).
5. M. FREJACQUES, *Bull. soc. franç. élec.*, **9**, 684 (1949).
6. A. VAYNA, *Alluminio*, **19**, 215 (1950).
7. V. P. MASHOVETZ, *J. Applied Chem. (U.S.S.R.)*, **9**, 789 (1936).
8. V. P. MASHOVETZ AND Z. F. LUNDINA, *Ukrain Akad. Nauk. Zapiski Inst. Khim.*, Sbornik Trudov Pervoi Vsesoyuznoi Konferentzii Nevodnuim Rastvoram, 191 (1935).
9. K. P. BATASHEV, *Trans. Leningrad Ind. Inst.*, **1**, 40 (1939).
10. G. AGNINI, *Chimica e industria (Milan)*, **22**, 209 (1940).
11. E. BONNIER AND J. L. ANDRIEUX, *Compt. rend.*, **231**, 1230 (1950).
12. J. W. FISCHER, *Z. anorg. u. allgem. Chem.*, **B20**, 17 (1948).
13. O. L. DAVIES, "Statistical Methods in Research and Production," p. 146, Oliver and Boyd, Edinburgh, Scotland (1949).
14. J. D. EDWARDS, F. C. FRARY, AND Z. JEFFRIES, "The Aluminum Industry: Aluminum and Its Production," p. 308, McGraw-Hill Book Co., Inc., New York, N. Y. (1930).
15. International Critical Tables, III, p. 24, McGraw-Hill Publishing Co., Inc., New York, N. Y. (1928).
16. F. WENNER, *Bull. Bur. Standards*, **8**, 559 (1912).
17. G. JONES AND S. M. CHRISTIAN, *J. Am. Chem. Soc.*, **57**, 272 (1935).

18. G. W. Vinal and D. N. Craig, *J. Research Natl. Bur. Standards*, **13**, 689 (1934) (Research Paper No. 738).
19. K. Arndt, *Z. Elektrochem.*, **12**, 337 (1906).
20. K. Arndt and A. Gessler, *Z. Elektrochem.*, **14**, 662 (1908).
21. E. K. Lee and E. P. Pearson, *Trans. Electrochem. Soc.*, **88**, 171 (1945).
22. R. W. Huber, E. V. Potter, and H. W. St. Clair, *Bureau of Mines*, Report of Investigations 4858, Washington, D. C.
23. W. Biltz and W. Klemm, *Z. physik. Chem.*, **110**, 318 (1924).
24. E. Ryshkewitch, *Z. Elektrochem.*, **39**, 531 (1933).
25. H. Bloom and E. Heymann, *Proc. Roy. Soc. (London)*, **188A**, 392 (1947).
26. J. O'M. Bockris and J. W. Tomlinson, *Research*, **2**, 362 (1949).

Conductivities and Densities of the System Ammonium Chloride—Zinc Chloride—Methanol from -50° to 20°C[1,2]

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ABSTRACT

Conductivities and densities have been determined for the concentrated electrolyte system, zinc chloride—ammonium chloride—methanol, over the temperature range from −50° to 20°C. From these data, it is possible to show that very extensive complex formation occurs in this system as a result of the presence of the zinc chloride. Certain features of the data are represented by empirical relations, but a complete description requires additional information which is not presently available.

Introduction

Although the use of concentrated solutions of electrolytes is prevalent in the electrochemical industry, there exists at the present time no adequate theoretical understanding of the physical behavior of such systems. The investigation summarized here represents a part of a program intended to accumulate comprehensive data which may help to lead to the development of quantitative theories applicable to concentrated systems.

Concentrated solutions of the zinc halides in methanol have been shown (1) to display characteristic variations in physical properties with changes in temperature and concentration which can be best explained on the basis of the formation of zinc polyhalide complexes in solution. The positions of the equilibria concerned, in methanol solution, have not yet been determined, but data are available to show the extent of such complex formation in water (2). Because it appears that complexing exerts a great influence on the conducting behavior of the simple zinc halides in methanol (1), it seemed desirable to obtain information on the extent to which such complex formation affects the conductivity of a relatively simple uni-univalent electrolyte in the same solvent.

Experimental

Methanol was dried by refluxing the 99.5 per cent commercial product over calcium oxide for 15 to 18 hours, distilling, refluxing over metallic calcium for from 8 to 10 hours, and distilling again. The entire operation was performed under nitrogen in order to prevent entry of either water or carbon dioxide.

Zinc chloride was purified from the C. P. grade by heating to a temperature just below its fusion point in a stream of dry hydrogen chloride for from 6 to 10 hours.

Ammonium chloride (A. R. grade) was dried by heating to 110°C for two hours and then stored in a desiccator.

Solutions for study were prepared in the following manner. Freshly dried zinc chloride was transferred quickly into anhydrous methanol and allowed to dissolve. Several such additions to the same batch of methanol were often required to obtain a sufficiently concentrated stock solution. When the stock was judged to be sufficiently concentrated (by qualitative observation of its approximate viscosity), it was assayed for chloride content by the Volhardt method. This stock was then used to prepare other zinc chloride solutions of the desired concentrations by dilution with methanol on a weight basis. The required amounts of ammonium chloride were then weighed into suitable aliquots of these zinc chloride solutions.

Conductances were measured by means of a Wheatstone bridge circuit using a Leeds & Northrup, Kohlrausch-type, slide-wire with headphones in a circuit containing a three-stage amplifier. The measurements were made at a frequency of 1000 cycles since over the range of specific conductances encountered in this study no difference in apparent conductance could be detected upon varying the frequency from 200 to 6000 cycles per second. A Washburn-type cell with platinized electrodes having a constant of 2.204 was used. The constant was determined by using standard potassium chloride solutions.

Densities were determined using a pycnometer which was a modified form of that described by Wright and Tartar (3). It consisted of a bulb to which was attached a calibrated large-bore capillary. Capacity of the apparatus was about 20 ml. The densitometer was calibrated above 0°C by use of

[1] Manuscript received May 7, 1951. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

[2] Based on research performed under contract No. W36-039-sc-38184 for the U. S. Army Signal Corps.

double-distilled water; at lower temperatures, methanol was used as a standard (4).

Discussion of Results

Tables I and II present the results of the determinations of specific conductance and of density, respectively. Data have been included for the simpler systems, ammonium chloride—methanol, and zinc chloride—methanol, in order to facilitate interpretation of the results for the mixed systems in terms of the Mixture Rule.

It should be noted specifically that the concentrations of all solutions are reported on a weight basis. This is done because the changes in volume concentration involved upon changing the temperature of a solution would lead to a different concentration value at each temperature and needlessly complicate the tabulations. The density data which are reported can be used to obtain the volume concentration at any of the experimental points by means of the formula,

$$C_1 = \frac{1000d}{\frac{1000}{m_1} + \frac{m_2 M_2}{m_1} + M_1} \qquad \text{(I)}$$

where C_1 is the concentration in moles per liter of solute component 1, m_1 is the concentration of solute component 1 in moles per thousand grams of solvent, M_1 is the formula weight of solute component 1, M_2 is the formula weight of solute component 2, m_2 is the concentration of solute component 2 in moles per thousand grams of solvent, and d is the density of the solution in grams per milliliter.

The densities are considered to be precise to within 0.2 per cent while the conductance values are precise to within 2.0 per cent or better. In the determination of the density for the mixed electrolyte solutions, it was observed that, in the solutions respectively 2.93 and 3.90 molal in zinc chloride, the densities of the systems containing ammonium chloride were the same as those of the simple zinc chloride solutions, regardless of the amount of ammonium salt present. The approach to this condition can be seen in the values given for the systems containing 2.09 molal zinc chloride, where at all concentrations of ammonium salt the densities for fixed temperatures are identical within the limits of experimental error. Therefore, the apparent molal volume of the ammonium chloride is equal to its molecular weight divided by the density of the zinc chloride solution.

In considering the conductivity data, isothermal plots of conductivity against concentration of one of the solutes are very informative. A consideration of the data in the simple system, zinc chloride—methanol, shows that such graphs have a conductivity maximum which occurs at progressively higher concentrations as the temperature is increased. Such plots will not be reproduced here because the tabular

TABLE I. *Conductivities of the system, zinc chloride—ammonium chloride—methanol*

$ZnCl_2$, Molality	Specific conductance ($\times 10^3$) at the temperatures,							
	20°C	10°C	0°C	−10°C	−20°C	−30°C	−40°C	−50°C
No NH_4Cl								
0.110	0.570	0.624	0.677	0.721	0.748	0.750	0.721	0.660
0.235	1.27	1.36	1.44	1.48	1.49	1.43	1.32	1.16
0.373	1.96	2.09	2.18	2.21	2.18	2.06	1.86	1.59
0.750	4.01	4.13	4.15	4.04	3.80	3.45	2.97	2.43
1.39	7.19	7.10	6.78	6.31	5.68	4.86	3.98	3.08
2.09	9.53	9.04	8.32	7.44	6.40	5.25	4.07	2.96
2.93	11.1	10.0	8.79	7.48	6.10	4.72	3.40	2.24
3.90	10.8	9.40	7.79	6.28	4.76	3.39	2.17	1.25
0.0985 Molal NH_4Cl								
0.00	4.65	4.13	3.64	3.17	2.73	2.30	1.90	1.49
0.110	4.42	3.92	3.45	3.02	2.62	2.23	1.87	1.53
0.235	4.54	4.09	3.66	3.30	2.96	2.61	2.24	1.85
0.373	4.72	4.36	4.04	3.75	3.43	3.06	2.64	2.18
0.750	6.12	5.89	5.60	5.24	4.80	4.23	3.57	2.87
1.39	8.79	8.43	7.88	7.22	6.42	5.46	4.43	3.38
2.09	10.6	9.96	9.06	8.03	6.92	5.64	4.35	3.16
2.93	11.9	10.7	9.34	7.91	6.44	4.95	3.57	2.31
3.90	11.6	9.93	8.20	6.59	5.02	3.55	2.29	1.32
0.244 Molal NH_4Cl								
0.00	9.48	8.43	7.40	6.46	5.55	4.66	3.82	3.03
0.110	9.17	8.14	7.13	6.21	5.32	4.48	3.64	2.88
0.235	8.96	7.94	6.96	6.05	5.21	4.39	3.59	2.86
0.373	8.86	7.86	6.94	6.09	5.31	4.53	3.76	3.03
0.750	10.2	9.28	8.35	7.50	6.58	5.66	4.68	3.69
1.39	11.1	10.3	9.44	8.49	7.43	6.27	5.05	3.83
2.09	12.4	11.4	10.3	9.11	7.71	6.30	4.84	3.49
2.93	13.2	11.9	10.3	8.79	7.13	5.46	3.93	2.58
3.90	12.6	10.9	8.98	7.16	5.49	3.87	2.53	1.47
0.310 Molal NH_4Cl								
0.00	11.3	10.0	8.82	7.70	6.60	5.55	4.55	3.57
0.110	11.0	9.78	8.60	7.50	6.40	5.40	4.38	3.45
0.235	10.7	9.53	8.35	7.25	6.22	5.21	4.22	3.32
0.373	10.6	9.41	8.25	7.18	6.21	5.23	4.30	3.41
0.750	10.8	9.76	8.73	7.78	6.85	5.84	4.83	3.80
1.39	12.2	11.2	10.2	9.09	7.96	6.63	5.32	4.02
2.09	13.3	12.1	10.8	9.52	8.06	6.57	5.04	3.64
2.93	13.5	12.1	10.5	8.77	7.12	5.48	3.93	2.58
3.90	13.1	11.2	9.25	7.41	5.64	4.03	2.63	1.51
0.388 Molal NH_4Cl								
0.00	13.4	11.9	10.5	9.15	7.74	6.55	5.36	4.15
0.110	13.1	11.6	10.2	8.86	7.60	6.36	5.16	4.05
0.235	12.7	11.3	9.92	8.61	7.37	6.14	4.97	3.88
0.373	12.7	11.2	9.81	8.51	7.30	6.10	4.94	3.88
0.750	12.5	11.2	9.94	8.74	7.62	6.43	5.26	4.11
1.39	13.5	12.3	11.0	9.78	8.47	7.05	5.64	4.26
2.09	14.2	13.0	11.5	10.1	8.53	6.91	5.30	3.81
2.93	14.7	13.1	11.3	9.48	7.76	5.91	4.23	2.79
3.90	13.7	11.7	9.65	7.71	5.90	4.17	2.77	1.59

TABLE II. *Densities of the system, zinc chloride—ammonium chloride—methanol*

$ZnCl_2$, Molality	Density (g/ml) at the temperatures,							
	20°C	10°C	0°C	−10°C	−20°C	−30°C	−40°C	−50°C
No NH_4Cl								
0.110	0.8013	0.8110	0.8207	0.8305	0.8400	0.8498	0.8596	0.8694
0.235	0.8133	0.8228	0.8325	0.8423	0.8520	0.8620	0.8719	0.8819
0.373	0.8254	0.8354	0.8454	0.8557	0.8650	0.8751	0.8852	0.8955
0.750	0.8589	0.8692	0.8795	0.8901	0.9000	0.9103	0.9209	0.9314
1.39	0.9154	0.9266	0.9376	0.9487	0.9592	0.9699	0.9807	0.9930
2.09	0.9731	0.9845	0.9961	1.0079	1.0186	1.0298	1.0409	1.0516
2.93	1.0446	1.0567	1.0688	1.0811	1.0920	1.1039	1.1150	1.1259
3.90	1.1181	1.1303	1.1431	1.1558	1.1667	1.1784	1.1902	1.2016
0.0985 Molal NH_4Cl								
0.00	0.7940	0.8032	0.8127	0.8224	0.8313	0.8408	0.8505	0.8601
0.110	0.8034	0.8129	0.8224	0.8322	0.8411	0.8507	0.8605	0.8705
0.235	0.8163	0.8245	0.8341	0.8441	0.8531	0.8629	0.8726	0.8829
0.373	0.8272	0.8369	0.8467	0.8568	0.8664	0.8761	0.8861	0.8966
0.750	0.8607	0.8708	0.8811	0.8916	0.9012	0.9117	0.9220	0.9321
1.39	0.9175	0.9282	0.9392	0.9504	0.9606	0.9713	0.9819	0.9931
2.09	0.9737	0.9848	0.9963	1.0079	1.0185	1.0291	1.0403	1.0517
0.244 Molal NH_4Cl								
0.00	0.7977	0.8070	0.8163	0.8260	0.8346	0.8442	0.8536	0.8635
0.110	0.8073	0.8166	0.8260	0.8356	0.8444	0.8538	0.8633	0.8732
0.235	0.8179	0.8272	0.8366	0.8465	0.8556	0.8651	0.8747	0.8848
0.373	0.8302	0.8395	0.8491	0.8590	0.8681	0.8779	0.8878	0.8981
0.750	0.8629	0.8730	0.8824	0.8932	0.9029	0.9129	0.9233	0.9338
1.39	0.9181	0.9297	0.9402	0.9514	0.9614	0.9720	0.9826	0.9937
2.09	0.9743	0.9854	0.9968	1.0084	1.0186	1.0302	1.0408	1.0515
0.310 Molal NH_4Cl								
0.00	0.8000	0.8033	0.8186	0.8281	0.8370	0.8463	0.8558	0.8653
0.110	0.8087	0.8180	0.8274	0.8371	0.8457	0.8551	0.8645	0.8744
0.235	0.8197	0.8290	0.8384	0.8483	0.8569	0.8662	0.8758	0.8857
0.373	0.8319	0.8412	0.8507	0.8605	0.8694	0.8792	0.8890	0.8990
0.750	0.8639	0.8735	0.8835	0.8939	0.9033	0.9136	0.9240	0.9342
1.39	0.9188	0.9297	0.9402	0.9514	0.9614	0.9720	0.9826	0.9937
2.09	0.9744	0.9856	0.9967	1.0084	1.0187	1.0302	1.0407	1.0518
0.388 Molal NH_4Cl								
0.00	0.8019	0.8111	0.8203	0.8299	0.8385	0.8479	0.8574	0.8668
0.110	0.8111	0.8202	0.8295	0.8393	0.8480	0.8571	0.8667	0.8764
0.235	0.8213	0.8306	0.8400	0.8496	0.8585	0.8679	0.8774	0.8873
0.373	0.8329	0.8424	0.8521	0.8616	0.8706	0.8800	0.8898	0.8999
0.750	0.8654	0.8751	0.8850	0.8951	0.9047	0.9147	0.9249	0.9356
1.39	0.9193	0.9301	0.9409	0.9519	0.9618	0.9725	0.9828	0.9939
2.09	0.9748	0.9860	0.9970	1.0087	1.0191	1.0301	1.0410	1.0520

data are most explicit on this point, and the question has been discussed in some detail elsewhere (1). In addition, it is apparent from the data that similar plots in the simple system, ammonium chloride—methanol, show a steady (although not linear) increase of conductivity with increasing concentration at all the temperatures investigated. Thus, it seems that in methanol, ammonium chloride behaves as an ordinary, well-dissociated electrolyte.

On the other hand, the conductivity of a system containing both of the electrolytic solutes shows a far more complicated behavior. If, to a solution containing ammonium chloride and methanol in a constant weight ratio, progressively increasing amounts of zinc chloride are added, the isotherms of conductivity as a function of the zinc chloride concentration develop an appearance of which the curves in Fig. 1 are representative examples. The first additions of zinc salt to the solution actually cause a marked decrease in the conductivity of the system, the concentration of zinc salt at which this drop is greatest being a function of both the temperature and the concentration of ammonium salt in the system.[3] Measurements of the location of this minimum conductivity are not especially precise, but by considering all the data, it is found that for a fixed temperature the ratio of zinc chloride, Z, to ammonium chloride, N, concentrations at this point is approximately constant, and that this ratio is empirically a

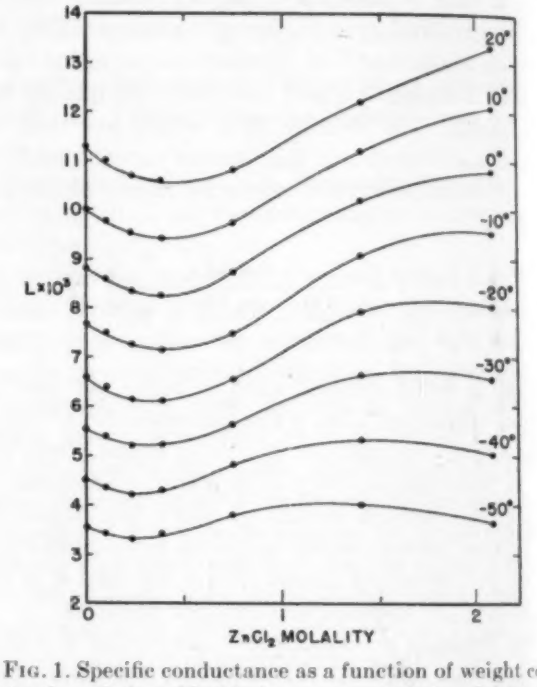

FIG. 1. Specific conductance as a function of weight concentration of zinc chloride in a system 0.310 molal in ammonium chloride with respect to anhydrous methanol as solvent.

[3] A simple calculation shows that this decrease is from 5 to 9 times greater than any that could be attributed to a simple volume dilution effect resulting from the addition of zinc chloride, even if zinc chloride were a nonelectrolyte.

function of temperature, T, according to the expression

$$\frac{Z}{N} = 0.0127T + 1.32. \qquad \text{(II)}$$

In a somewhat similar manner, it is also seen that the depth of the conductivity drop (difference between conductivity at zero zinc chloride concentration and that at concentration, Z) becomes smaller as temperature diminishes. Holding the ammonium chloride concentration constant, it is found that this depth, L, is an approximately linear function of temperature. Then considering the coefficients of such temperature dependent functions as themselves being functions of N, it is found that they, too, are approximately linear functions of N within the limits of error of the measurements. Hence, by successive graphical constructions, it is possible to arrive at the empirical expression

$$L = 2 \cdot 10^{-6}(T) + 1.5 \cdot 10^{-5}(NT) + 2 \cdot 10^{-3}(N) \qquad \text{(III)}$$

for the dependence of the depth of the minimum (or conductivity drop) on both temperatures and concentrations, since N and Z are related by equation (II).

When one attempts to proceed beyond such empirical descriptions of the data, however, the situation is too complex to be amenable to complete theoretical treatment on the basis of the available experimental information. The simplest approach to such a treatment would be found in the application to the data of the simple Mixture Rule for conductivities (5). According to this rule, the conductivity of a mixture of electrolytes should be equal to the sum of the conductivities of the individual components. It has been shown, however, that even in aqueous solutions of highly dissociated mixed electrolytes marked deviations from such a rule occur frequently (6–10). In the case of the highly ionized mixtures, where there is no possibility of the formation of ionic complexes, a theoretical development (5) based on the mobilities of the conducting species has been very successful in accounting for the observed variations, while the case of mixtures in which complex formation of a predictable kind enters into the considerations can be treated satisfactorily also by the introduction of the mass action equilibria (11). However, these procedures require both transference and equilibrium constant data for the system in question, and such information appears to be entirely lacking for nonaqueous systems such as the one now being discussed. Some progress might be made in supplying this deficiency by using procedures (12–15) which permit conversion of data obtained in aqueous solutions for use in other solvent media. However, all of the available methods can be applied only in relatively dilute solutions, and even then only when the formation of ionic complexes does not enter into the calculations.

Because of these limitations, it appears that a complete application of available theory to the present data must await accumulation of additional information concerning the specific system in question. It is possible, however, to deduce something of the nature of the present mixed electrolyte system by a simple consideration of the deviations from the ordinary Mixture Rule which it displays. Fig. 2 and 3 show examples of these deviations under two extremes of conditions; in Fig. 2 is shown the behavior of a system, containing a very small quantity of ammonium chloride, at the lowest temperature studied, while Fig. 3 shows the system containing nearly a saturation amount of ammonium chloride at the highest temperature studied. In both figures, curve I gives the conductivity of the ammonium chloride at a constant molality. The small negative slope occurs because of the fact that the conductivity itself is directly dependent upon volume concentration which will change with addition of the second solute, even though the weight concentration remains the same. Curve II gives the conductivity

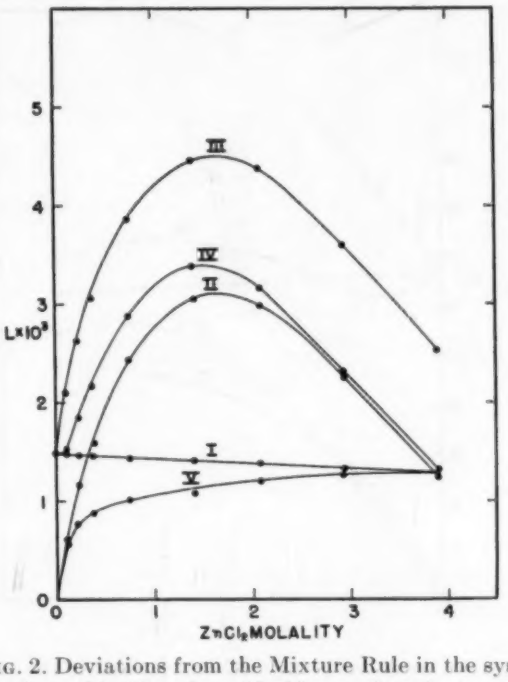

FIG. 2. Deviations from the Mixture Rule in the system ammonium chloride—zinc chloride—methanol at −50°C. I—0.0985 molal ammonium chloride; II—zinc chloride, no ammonium chloride; III—prediction by the Mixture Rule for 0.0985 molal ammonium chloride with zinc chloride added; IV—experimental conductivity for 0.0985 molal ammonium chloride with zinc chloride added; V—deviation of experimental conductivities from those predicted by the simple Mixture Rule.

of the zinc chloride as a function of concentration. Curve III represents the calculated sum of curves I and II which is the conductivity predicted for the mixed system by the simple Mixture Rule. Curve IV shows the actual conductivity of the mixed system, while curve V indicates the magnitude of the deviation from the simple Mixture Rule, being the difference between curves III and IV.

Considering first Fig. 3, it is seen that the experimental conductivities for the mixed system at zinc chloride concentrations below one molal fall markedly lower than the conductivity of even the simple ammonium chloride solution alone. This behavior is confirmed by the other curves for similar systems and can be interpreted only as demonstrating that the addition of the zinc salt removes relatively mobile chloride ions from solution by means of complex formation, replacing them with less mobile zinc polychloride anions. Reference to Fig. 2 supports this conclusion. There, it may be observed that for additions of zinc chloride up to about 0.1 molal the conductivity remains relatively constant in the vicinity of that of the ammonium salt alone, despite the fact that the simple Mixture Rule predicts a steep increase in this region. At concentrations of zinc salt above 0.1 molal, the conductivity increases fairly rapidly in the manner, though not in the magnitude, predicted by the Mixture Rule, and at the highest concentrations the conductivity for the mixed system becomes almost identical with that of the simple zinc chloride solution alone. Again the best available interpretation of this behavior seems to be the conclusion that the zinc salt essentially cancels the effect of the ammonium chloride as a separate conducting species. If this conclusion is correct, then it should appear that diminution of the temperature should enhance the effects observed by adding stability to the zinc polyhalide internal bonding. This is actually observed, the only case where virtually complete identity of the mixed electrolyte curve with that of the zinc salt alone occurring at −50°C in the system containing the smallest amount of ammonium chloride.

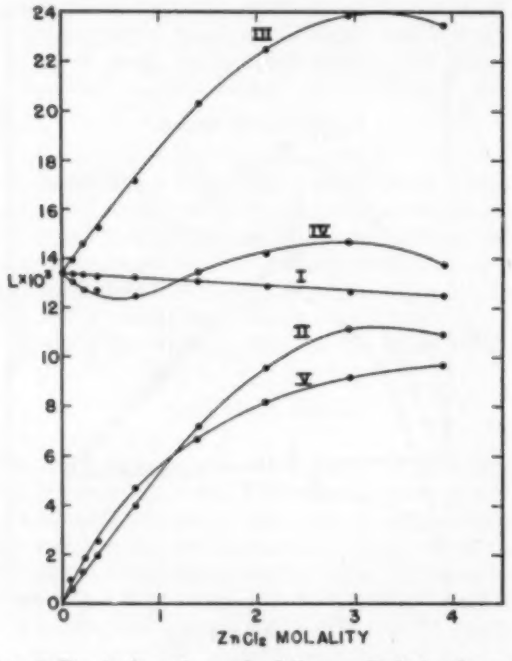

FIG. 3. Deviations from the Mixture Rule in the system ammonium chloride—zinc chloride—methanol at 20°C. I—0.388 molal ammonium chloride, no zinc chloride; II—zinc chloride, no ammonium chloride; III—prediction of the Mixture Rule for 0.388 molal ammonium chloride with zinc chloride added; IV—experimental conductivity for 0.388 molal ammonium chloride with zinc chloride added; V—deviation of experimental conductivities from those predicted by the simple Mixture Rule.

In terms of the deviations of the experimentally determined conductivities from those predicted by the Mixture Rule, it appears that these deviations approach the conductivity of the simple ammonium chloride solutions in all cases, but that the closeness of this approach becomes progressively decreased as the temperature is increased and as the amount of available ammonium salt becomes greater. This can be regarded only as powerful evidence of the very great complexing power of the naturally acidic (in the Lewis sense) zinc ion. It might be added that the same kind of reasoning leads to the conclusion that in methanol solutions ammonium chloride behaves as a relatively strong electrolyte.

In addition to these qualitative conclusions concerning the nature of the conducting species in this system, it should be noticed that the presence of lower concentrations of the zinc salt in solutions of ammonium chloride has a very marked effect upon the over-all temperature coefficient of conductivity, tending in the solutions most dilute in ammonium chloride to decrease the drop in the conductivity of the solution with falling temperature.

This moderating influence exerted by the zinc salt well may find practical application in the design of systems in which it is desired to keep the conductance at a relatively constant level over a rather broad range of temperatures.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. L. R. DAWSON, A. TOCKMAN, H. K. ZIMMERMAN, JR., AND G. R. LEADER, *J. Am. Chem. Soc.*, **73**, 4327 (1951).
2. L. G. SILLEN AND B. LILJEQVIST, *Svensk Kem. Tid* **56**, 85 (1944).

3. K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 544 (1939).
4. Landolt-Börnstein-Roth Tabellen, 5th ed., Vol. I, p. 452, Julius Springer, Berlin (1923).
5. P. Van Rysselberghe and L. Nutting, *J. Am. Chem. Soc.*, **56**, 1435 (1934).
6. A. E. Stearn, *J. Am. Chem. Soc.*, **44**, 670 (1922).
7. C. E. Ruby and J. Kawai, *J. Am. Chem. Soc.*, **48**, 1119 (1926).
8. A. K. Smith and R. A. Gortner, *J. Phys. Chem.*, **37**, 79 (1933).
9. P. Van Rysselberghe and L. Nutting, *J. Am. Chem. Soc.*, **59**, 333 (1937).
10. P. Van Rysselberghe, S. W. Grinnell, and J. M. Carlson, *J. Am. Chem. Soc.*, **59**, 336 (1937).
11. C. W. Davies, *J. Chem. Soc.*, **1938**, 448.
12. H. Uhlich, *Trans. Faraday Soc.*, **23**, 388 (1927).
13. H. Hartley and H. R. Raikes, *Trans. Faraday Soc.*, **23**, 293 (1927).
14. B. B. Owen, *J. Am. Chem. Soc.*, **57**, 2441 (1935).
15. T. Shedlovsky, *J. Chem. Phys.*, **6**, 845 (1938).

The Nature of the Films Formed by Passivation of Iron with Solutions of Sodium Phosphate[1, 2]

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ABSTRACT

The weights of ferric phosphate present in films formed by the passivation of iron in 0.1*M* solutions of disodium and trisodium phosphate were determined using a radioactive tracer, and the thickness of oxide was estimated by an electrochemical method. The weights of phosphate were found to decrease with a rise in *p*H value of the solution. Surface pretreatments, involving the removal of the original air-formed oxide film by dipping in acid, resulted in higher phosphate contents than surface pretreatments involving abrasion, either with or without subsequent prolonged exposure to dry air.

Introduction

As early as 1836 Faraday suggested (1) that the passivity of iron in concentrated nitric acid was due to a thin invisible protective oxide film. Subsequently Evans (2, 3) isolated the films formed on freshly abraded iron which had been passivated in potassium chromate solution, and showed that they were not appreciably attacked by 0.1*N* hydrochloric acid; he concluded that these films consisted of anhydrous ferric oxide as distinct from the hydrated product.

A recent electron microscope/electron diffraction study of the surface films formed by passivation of iron by disodium phosphate saturated with dissolved air (4) showed that these films were composed largely of γ-Fe_2O_3, but also contained inclusions of $FePO_4 \cdot 2H_2O$. The size of the inclusions varied greatly, the larger particles having a diameter of the order of 1 μ.

It was subsequently shown (5) by weight loss determinations, polarization, and electrode potential measurements, both in the presence and absence of dissolved air, that iron can be passivated by phosphate solutions only when these contain dissolved air. Passivation was accordingly ascribed to the formation of a thin film of γ-Fe_2O_3 which was believed to take of the order of 24 hours to attain a protective character. It was suggested that, during the early stages of passivation, the formation of γ-Fe_2O_3 was accompanied by slow corrosion leading to the production of $FePO_4 \cdot 2H_2O$. It was further suggested that the electrochemical action must be under anodic control owing to the small dimensions of the anodic areas.

It appears desirable, therefore, to determine whether there is any relationship between the concentration of phosphate in the passivity films, the *p*H of the solution, and the surface pretreatment of the specimen. Since the films formed during passivation are only of the order of 200 Å thick and the quantity of phosphate is likely to be only a few per cent of the total film, its accurate determination by normal micro-analytical methods is difficult. Consequently, it was decided to use a tracer technique involving the use of a small quantity of P^{32} in the passivating solutions.

Experimental

Materials.—The iron used was in the form of annealed sheet 0.02 cm thick; it was kindly supplied by the British Iron & Steel Research Association, and had the same composition as previously described (5).

Specimens measuring 3 x 1 cm were cut from the sheet and thoroughly degreased in benzene.

Two stock solutions of 0.1*M* Na_2HPO_4 and 0.1*M* Na_3PO_4 were prepared from C.P. chemicals, distilled water, and a sufficient quantity of pure P^{32} (half-life 14.1 days), in the form of phosphate, to give an activity of approximately 1 millicurie per ml of solution. The stock solutions had *p*H values of 9.1 (Na_2HPO_4) and 12.2 (Na_3PO_4); they were shaken thoroughly in contact with the atmosphere

[1] Manuscript received June 30, 1951. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952. The authors have kindly consented to a delay in publication so that this paper may appear in the special Theoretical Electrochemistry Issue of the Journal.

[2] From a thesis submitted by L. J. Stagg to the Graduate School of Louisiana State University in partial fulfillment of the requirements for the degree of Master of Science.

to ensure saturation with dissolved air. If this precaution was not observed, very erratic results were obtained.

The specimens were given one of 3 surface pretreatments:

1. Dipped in 0.2*N* HCl for 15 sec, washed rapidly in distilled water and immediately immersed in the passivating solution.
2. Abraded with 3/0 emery paper, swabbed with benzene, and immediately immersed in the passivating solution.
3. Abraded with 3/0 emery paper, swabbed with benzene, and stored in dry air for 24 hours before immersion in the passivating solutions.

All experiments were carried out in duplicate.

Experimental method.—In a typical experiment, the specimen was totally immersed in 5 ml of the passivating solution for 24 hours with its upper edge 1 cm below the waterline of the solution. At the end of this period, it was removed from solution and washed thoroughly with distilled water until the washings showed no evidence of radioactivity when monitored with an end-window Geiger counter. The specimen was then dried and rubbed with filter-paper; the filter-paper was monitored and, if it showed signs of activity, the washing and drying process was repeated until neither the washings nor the filter-paper showed signs of activity; these precautions were taken to avoid the carry-over of activity from the passivating solution.

The oxide film on the specimen was then reduced to ferrous ions by cathodic treatment for 60 sec in 3 ml of 0.2*N* HCl at a current density of 3 ma/cm², which was sufficiently high to protect the specimen once the passivity film was reduced; platinum wire was used as an anode. The *p*H of the solution was also sufficiently low to dissolve most of the ferric phosphate present in the film. As a precaution against adsorption of the radioactive phosphate on the walls of the glass vessels used, 10^{-4} g of inactive phosphate was added to the original acid solution. This would reduce any adsorption of radioactive phosphate by a factor of approximately 10. After cathodic treatment for 60 sec, the current was discontinued and the specimen washed, the washings being added to the solution which was then made up to 5 ml (solution A).

When monitored with an end-window Geiger counter the specimen still showed activity and accordingly was immersed for 15 sec in 3 ml of 1:1 HCl to which had been added 10^{-4} g of inactive phosphate to reduce any adsorption of radioactive phosphates. After this treatment, the specimen showed no sign of radioactivity. The residual solution was then made up to 5 ml (solution B).

The radioactivity of the solutions was measured as follows: an aliquot was pipetted onto an aluminum counting disk upon which a drop of concentrated ammonium hydroxide solution had previously been placed. This ammonia served to neutralize the acid in the phosphate solution which otherwise would attack the aluminum; excess ammonia volatilized when the disk was dried. In the case of solution (A) the aliquot was 200 μl; in the case of solution (B) the aliquot was only 50 μl since, owing to the high acid content of this solution, the residue of ammonium chloride on the disk was considerable. Such a residue would cause appreciable selfabsorption of

TABLE I. *Composition and thickness of films*

Surface treatment of specimen	Passivating solution	Wt of $FePO_4 \cdot 2H_2O$ obtained by reduction of film in 0.2*N* HCl, mg	Wt of residual $FePO_4 \cdot 2H_2O$, mg	Total weight of $FePO_4 \cdot 2H_2O$ in the film, mg	Wt of oxide on specimen, mg	Wt % of phosphate in total film	Estimated thickness of oxide film, Å
Dipped in 0.2*N* HCl for 15 sec to remove air-formed oxide film	0.1*M* Na_2HPO_4	11.0×10^{-3}	4.8×10^{-3}	15.8×10^{-3}	60×10^{-3}	21	200
		10.3×10^{-3}	4.7×10^{-3}	15.0×10^{-3}	30×10^{-3}	34	95
	0.1*M* Na_3PO_4	6.2×10^{-3}	2.3×10^{-3}	8.5×10^{-3}	60×10^{-3}	12	200
		4.3×10^{-3}	1.9×10^{-3}	6.3×10^{-3}	30×10^{-3}	17	100
Abraded with 3/0 emery and immediately immersed in the passivating solution	0.1*M* Na_2PHO_4	3.7×10^{-3}	0.58×10^{-3}	4.3×10^{-3}	60×10^{-3}	6.7	200
		3.5×10^{-3}	0.62×10^{-3}	4.1×10^{-3}	55×10^{-3}	6.9	185
	0.1*M* Na_3PO_4	1.6×10^{-3}	0.59×10^{-3}	2.2×10^{-3}	71×10^{-3}*	3.0	240
		1.1×10^{-3}	0.16×10^{-3}	1.3×10^{-3}	52×10^{-3}	2.4	175
Abraded with 3/0 emery and stored in dry air for 24 hours before immersion in the passivating solution	0.1*M* Na_2HPO_4	3.6×10^{-3}	0.42×10^{-3}	4.0×10^{-3}	45×10^{-3}	8.1	150
		3.1×10^{-3}	0.86×10^{-3}	3.9×10^{-3}	48×10^{-3}	7.4	160
	0.1*M* Na_3PO_4	1.2×10^{-3}	0.13×10^{-3}	1.3×10^{-3}	31×10^{-3}	4.0	100
		0.54×10^{-3}	0.62×10^{-3}	1.2×10^{-3}	45×10^{-3}	2.5	150

* Abnormally high iron content due to slight corrosion of the iron during the washing process.

the β-particles unless kept to a minimum. These sources were counted by means of an end-window Geiger counter (window = 1.8 mg/cm² mica) and the measurements corrected for radioactive decay and background count. Counting rates ranged from approximately 200–4500 counts/min and the counting times were such as to obtain at least 4000 counts. A standard Co^{60} source was used to check the efficiency of the counter; no significant variation in efficiency occurred during the experiments. Sources were also prepared from the original stock solutions and by comparison of the total corrected counts from a fixed volume of solution the weight of phosphate in the film was determined.

The iron content of the solution obtained by reduction of the film was determined colorimetrically using the thioglycollic acid method (7). By subtracting the weight of iron equivalent to the measured concentration of phosphate in the solution, the weight of iron due to the reduction of γ-Fe_2O_3 and hence the weight of oxide in the film was calculated.

The results of these experiments are shown in Table I. The thicknesses of the oxide films were estimated using the apparent area of the specimens and an approximate figure of 5 g/cc for the density of γ-Fe_2O_3.

Discussion

The fact that appreciable quantities of phosphate are found in the passivity films confirms the suggestion that slow electrochemical attack takes place on the iron during the early stages of passivation. Oxygen dissolved in solution reacts with the surface of the iron, resulting in the formation of a thin film of γ-Fe_2O_3, which must be primarily responsible for passivity, since it has been demonstrated by Pryor and Cohen (5, 6) that if the passivating solutions are deaerated, the iron suffers slow electrochemical corrosion. The presence of the phosphate must be ascribed to the fact that the oxide film takes an appreciable time to build up to a sufficient degree of thickness or continuity to prevent corrosion.

Experiments were carried out in which specimens were exposed to dry air for periods of six hours and one week. The thickness of the oxide films was determined as described above and values of 127 Å and 130 Å, respectively, obtained. Since the thickness of oxide films formed during passivation is of this order and their composition is the same, i.e., γ-Fe_2O_3, it is considered that oxide films are formed in passivating solutions in a manner similar to that by which oxide films are formed in air. Furthermore, this heterogeneous reaction should be independent of the *p*H value of the solution.

It is clear from the table that both the weights and percentages of ferric phosphate in the passivity films are greater in disodium phosphate than in trisodium phosphate. Since the ferric phosphate is formed as a result of the initial electrochemical corrosion, its quantity is a measure of the total corrosion current flowing once precipitation has started. It was demonstrated previously (5) that, in phosphate solutions saturated with dissolved air, the anodic polarization became greater with an increase in *p*H at constant total phosphate content; this polarization was believed the result of contraction of the anodic areas due to growth of the oxide rather than precipitation of ferric phosphate. Furthermore the cathodic polarization (largely of the reduction of dissolved oxygen) was little influenced by a change in *p*H. It follows, therefore, that the rate of the initial corrosion will decrease with a rise in *p*H value of the solution. Furthermore, it was pointed out that the electrochemical formation of phosphate during passivity was under anodic control due to the small size of the areas available for anodic action. This latter statement may appear surprising in view of the comparatively high weights of ferric phosphate found in some of the films, but it was previously suggested (5) that the phosphate is more permeable to the diffusion of iron ions than γ-Fe_2O_3. Consequently the inclusions of phosphate will thicken more rapidly than the oxide film. The ferric phosphate, therefore, will not be distributed uniformly through the film but will be concentrated at the sites of the initial corrosion where its thickness will be greater than that of the surrounding oxide film. As the inclusions or "plugs" of phosphate thicken, their resistance to the diffusion of iron ions will increase, with the result that further precipitation of phosphate will become progressively slower. Equilibrium is apparently attained after approximately 24 hours when the thickness of oxide and phosphate is sufficient to prevent further detectable corrosion. It should be emphasized once more, however, that the ferric phosphate by itself does not form a protective film and that the thin film of oxide is primarily responsible for passivity.

It may also be seen that the weights of phosphate are comparatively reproducible, but that the weights of oxide have a much greater scatter. This may be due to the fact that the distribution of sodium phosphate in the passivating solution is likely to be more uniform than that of dissolved oxygen.

The effect of varying the surface treatment of the specimens is less striking than that of *p*H. However, it appears that the pretreatment involving dipping in hydrochloric acid results in much higher phosphate contents than pretreatments involving abrasion. Presumably the surface, being initially largely free from oxide, has many more sites available for electrochemical action. Furthermore, the compara-

tively high initial rates of corrosion may also lead to precipitation of ferric phosphate on the surface of the oxide. In comparing experiments in which abraded specimens were either immediately immersed or allowed to grow an oxide film in air for 24 hours before immersion, it can be seen that the weight of phosphate is greater in the former experiments, but that the oxide film grows to a greater thickness. This results in the percentage of phosphate being generally smaller in films formed on freshly abraded specimens. Apparently there is little further growth of oxide in specimens that have been allowed to form a relatively thick air-formed oxide film prior to immersion in the passivating solution.

The determinations carried out confirm the conclusions of the previous electron diffraction study (4) which indicated that the passivity films formed in solutions of sodium orthophosphates are duplex. The phosphate is considered to be the result of slow electrochemical action during the early stages of oxide film formation, when the film is not sufficiently thick and/or continuous to prevent corrosion. Thus when an iron specimen is immersed in a passivating phosphate solution two reactions take place simultaneously:

(*A*) Direct formation of γ-Fe_2O_3 by oxygen dissolved in solution.

(*B*) Initial electrochemical attack at discontinuities in this oxide film resulting in the formation of relatively thick "plugs" of $FePO_4 \cdot 2H_2O$.

The subsequent behavior of the specimen is largely determined by factors influencing reaction (*B*) since reaction (*A*) should only be affected by the partial pressure of oxygen in the solution and the surface condition of the iron. Any factor which increases the rate of (*B*) will lead to an enhanced initial rate of corrosion and will militate against ultimate passivity.

Evidence of the duplex nature of films formed in sodium hydroxide (8) and sodium nitrite (9) has also been obtained during the electron diffraction studies of the authors and their co-workers. In these cases, however, the second constituent is γ-FeO·OH-lepidocrocite. It appears probable, since the potential/time curves of iron immersed in these inhibitors are so similar to those obtained in sodium orthophosphates, that the passivity films are built up in a similar manner to that described above.

Summary

Films formed during passivation of iron in solutions of sodium orthophosphates containing dissolved air have been shown to contain some ferric phosphate in addition to γ-Fe_2O_3. The quantity of phosphate decreases with a rise in *p*H at constant phosphate content, being about half as great in 0.1*M* Na_3PO_4 (*p*H = 12.2) as in 0.1*M* Na_2HPO_4 (*p*H = 9.1). Surface pretreatments involving destruction of the original air-formed oxide film by dipping in acid result in high phosphate contents compared with surface treatments involving abrasion at similar *p*H values. The equilibrium thickness of γ-Fe_2O_3 also formed during passivation is similar to that resulting from exposure of iron to dry air.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. C. T. SCHÖNBEIN AND M. FARADAY, *Phil. Mag.*, **9**, 53, 57 (1836).
2. U. R. EVANS, *J. Chem. Soc.*, **1927**, 1020.
3. U. R. EVANS, *Trans. Am. Inst. Mining Met. Eng.*, **1929**, 7.
4. J. W. MENTER, Compt. rend. du Premier Congrès International de Microscopie Électronique, Paris 1950. Éditions de la Revue d'Optique, Paris 1952.
5. M. J. PRYOR AND M. COHEN, *J. Electrochem. Soc.*, **98**, 263 (1951).
6. M. J. PRYOR AND M. COHEN, *Nature*, **167**, 157 (1951).
7. J. W. SWANK AND M. G. MELLON, *Ind. Eng. Chem.* (*Anal*), **30**, 7 (1938).
8. J. E. O. MAYNE, J. W. MENTER, AND M. J. PRYOR, *J. Chem. Soc.*, **1950**, 3229.
9. M. COHEN, *J. Phys. Chem.*, **56**, 451 (1952).

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A Polarographic Method for the Indirect Determination of Polarization Curves for Oxygen Reduction on Various Metals

III. Chromium, Molybdenum, Tantalum, Titanium, Tungsten, and Zirconium[1]

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ABSTRACT

Polarization curves for the electrolytic reduction of oxygen are determined for several metals by application of a polarographic method previously described (1). The contributions of the two and four electron processes, i.e., reduction of oxygen to hydrogen peroxide and to water, respectively, are determined. The electrolytic reduction of oxygen on chromium, tantalum, titanium, and tungsten may yield appreciable quantities of hydrogen peroxide. Very little hydrogen peroxide is formed on zirconium and molybdenum.

INTRODUCTION

An indirect method for the determination of the polarization curves corresponding to a single electrode process was recently reported (1) and applied to the study of the reduction of oxygen on various metals (1) and to related corrosion processes (2). In the present paper, the method is applied to the reduction of oxygen on six of the less common metals. In this indirect method, the electrode, on which the oxygen reduction is studied, is polarized at a constant potential in a closed vessel containing a solution initially saturated with air. The concentration of oxygen is measured by the polarographic method in the course of time, and the polarization current corresponding to the reduction of oxygen at the metal surface is calculated from the oxygen concentration-time curve. The complete polarization curve is obtained by repeating the experiment for several potentials. The reduction of oxygen at a given potential is characterized by its apparent number of electrons n which is defined as follows (1):

$$n = 2 + 2\left(\frac{\text{Amount of oxygen reduced at time } t \text{ in the four-electron process}}{\text{total amount of oxygen reduced at time } t}\right).$$

The value of n at a given potential is calculated from the polarographic data thus obtained. The experimental method and the calculations of the polarization curve have been previously reported (1) and no further details are needed here. All the measurements were carried out in a phosphate buffer at *p*H 6.9 (1).

EXPERIMENTAL RESULTS AND DISCUSSION

Chromium

The polarization current for the reduction of oxygen and the apparent number of electrons involved in the reduction of oxygen are plotted against potential in Fig. 1. Since the apparent number of electrons is close to two over a wide range of potentials, hydrogen peroxide may be formed at a chromium electrode with almost theoretical efficiency. In the neighborhood of −0.4 volt there is a rather rapid transition from the two-electron process to the four-electron process, and the current increases accordingly. The overvoltage for the reduction of oxygen to water is smaller than that for most of the common metal previously studied (1). From this point of view, chromium behaves as iron although the chromic-chromous couple does not catalyze the decomposition of hydrogen peroxide, whereas the ferric-ferrous couple does. This results from the fact that the potential for the Fe^{+3}-Fe^{+2} couple (E_0 = 0.77 volt) (3) is comprised between the potential for the H_2O_2-H_2O (E_0 = 1.77 volts) and O_2-H_2O_2 (E_0 = 0.68 volt) couples whereas the potential of the Cr^{+3}-Cr^{+2} couple (E_0 = −0.41 volt) is not. In the case of the Fe^{+3}-Fe^{+2} couple, hydrogen peroxide is oxidized to oxygen by Fe^{+3}, and the ferrous derivative resulting from this reaction is reoxidized by hydrogen peroxide. In the case of the Cr^{+3}-Cr^{+2} couple these reactions do not occur.

The values of the apparent number of electrons n at −1.13 and −1.26 volts (vs. N.H.E.) (see Fig. 1) are smaller than 4. This is rather unexpected since n is equal to 4 at less negative potentials. The decrease of n at high negative potentials is possibly

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related to the evolution of relatively large quantities of hydrogen at the electrode. However, it seems difficult to postulate a plausible mechanism accounting for the decrease of n.

Tantalum

The data of Fig. 2 show that the behavior of tantalum in the electrolytic reduction of oxygen is somewhat similar to that of chromium. However,

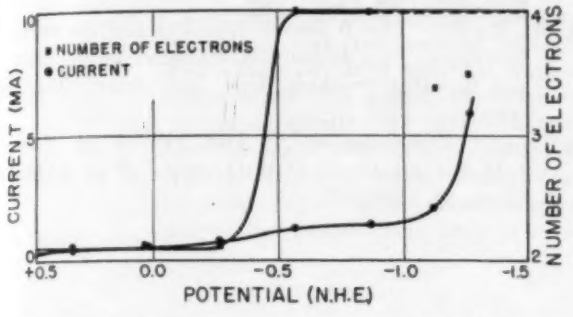

FIG. 1. Polarization curve and apparent number of electron-potential curve for the reduction of oxygen on chromium.

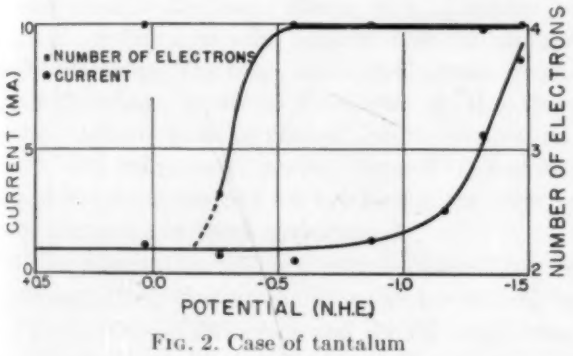

FIG. 2. Case of tantalum

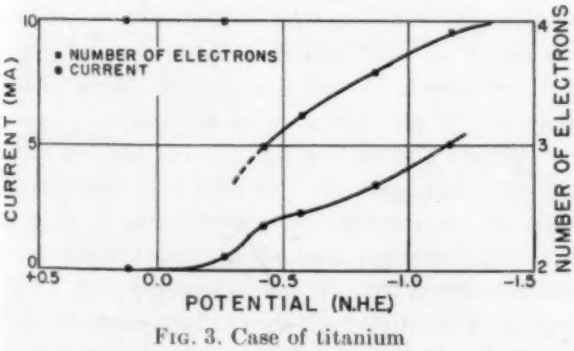

FIG. 3. Case of titanium

experimental results were erratic and the catalytic decomposition of hydrogen peroxide was very pronounced at slightly positive potentials (vs. normal hydrogen electrode).

Titanium

The case of titanium (Fig. 3) is similar to that of silver (1). Appreciable quantities of hydrogen peroxide may be produced at potentials between −0.4 and −1 volt (vs. N.H.E.). At potentials less negative than −0.4 volt the catalytic decomposition of hydrogen peroxide maintains the concentration of that substance at a very low limit.

Tungsten

Tungsten favors somewhat the production of hydrogen peroxide (Fig. 4) although more than 50 per cent of the oxygen is at least reduced to water. In this respect, tungsten is comparable to platinum (1).

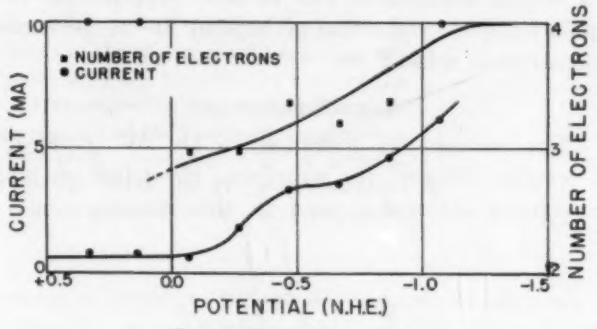

FIG. 4. Case of tungsten

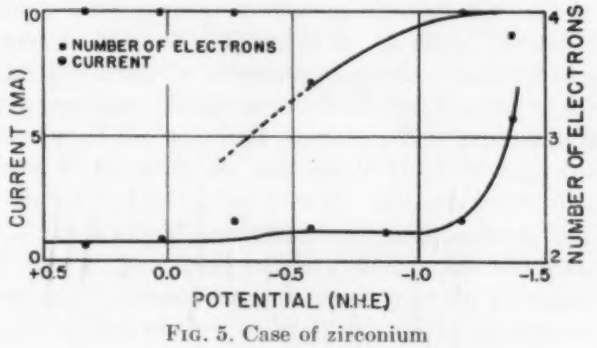

FIG. 5. Case of zirconium

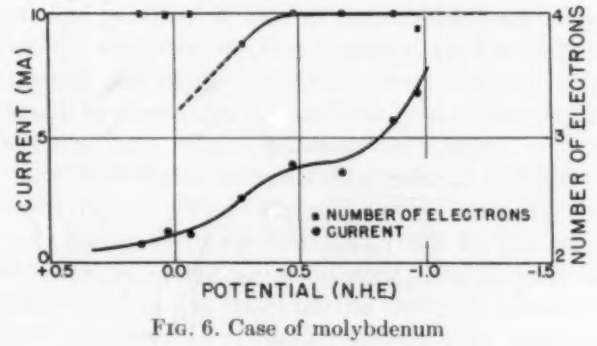

FIG. 6. Case of molybdenum

Zirconium and Molybdenum

These metals do not favor the production of hydrogen peroxide (Fig. 5 and 6). This may be explained as follows. First, it may be assumed that the overvoltages for the reduction of oxygen to hydrogen peroxide and for the reduction of hydrogen peroxide to water are such that practically no hydrogen peroxide can be formed on the electrode (1). Another explanation is that the reduction of hydrogen peroxide to water is "catalyzed" by the intermediate formation of a peroxyderivative of zirconium or

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molybdenum. Such a compound would be formed by reaction of hydrogen peroxide with the oxide or hydrated oxide covering the surface of the metal (4). In the next step, the peroxyderivative would be reduced with the formation of water. Thus, the reduction of oxygen to water with the intermediate formation of a peroxyderivative would occur at a potential at which oxygen would be reduced to hydrogen peroxide in the absence of a peroxyderivative. A similar mechanism was recently proposed for the polarographic reduction of oxygen in the presence of carbonic acid (5).

Acknowledgment

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REFERENCES

1. P. DELAHAY, *J. Electrochem. Soc.*, **97**, 198, 205 (1950).
2. R. H. BROWN, G. C. ENGLISH, AND R. D. WILLIAMS, *Corrosion*, **6**, 186 (1950).
3. W. M. LATIMER, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York (1938).
4. W. MACHU, "Das Wasserstoffperoxyd und die Perverbindungen," pp. 49 and 238, Springer, Vienna (1937), and Edwards Brothers, Inc., Ann Arbor, Michigan (1944).
5. P. VAN RYSSELBERGHE, P. DELAHAY, A. H. GROPP, J. M. MCGEE, AND R. D. WILLIAMS, *J. Phys. & Colloid Chem.*, **54**, 754 (1950).

Primary Current Distribution Around Capillary Tips Used in the Measurement of Electrolytic Polarization[1]

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ABSTRACT

Equipotentials have been mapped out around the electrode and the tip of the capillary for the following arrangements: (*a*) capillary in front of the electrode; (*b*) capillary behind a finite electrode having an insulated back; (*c*) capillary through the back of the electrode and having its tip at the front surface. Arrangement (*a*) can be used for accurate measurements if the distance between the electrode and the capillary tip of radius r is $4r$ or more, and any appreciable IR drop subtracted. Arrangement (*b*) is unsatisfactory because the current density varies over the surface of the electrode. With arrangement (*c*) the current density is increased at the area nearest the capillary, hence the polarization measurement tends to be too high.

INTRODUCTION

In the study of electrolytic polarization it is important to measure the polarization (the change in electrode potential resulting from current flow) at known current densities. Hence it is desirable to maintain uniform current density over the surface of the electrode. The most suitable electrode geometries are those sectioned from one of the three systems: infinite parallel planes, infinite coaxial cylinders, and concentric spheres. Kasper (1) has discussed the requirements for producing the electrolytic analogues of these systems.

If the polarization at one electrode of a cell can be made negligible, that at the other is determined by the total potential difference and the IR drop across the cell. Such cells are readily achieved using coaxial cylinders or concentric spheres, since the current density at the outer electrode may be made extremely small. With plane parallel electrodes, it is generally impossible to maintain one of the electrodes unpolarized. In the well-known Haring cell (2), however, this difficulty is circumvented by the insertion of plane screen probes between the electrodes; measurement of the total potential difference and IR drop between an unpolarized screen and the electrode under study yields the polarization voltage.

There are three methods of measurement which, as ordinarily carried out, do not include the evaluation of IR drops. The potential of the polarized electrode is determined by comparison with an external reference (constant potential) electrode which is connected to the cell through a tube of electrolyte.[2]

1. Direct method: The potential measurement is made while current is flowing through the cell. In order to prevent inclusion of an IR drop, the end of the tube from the reference electrode is reduced to a fine capillary, the tip of which is brought close to the surface of the polarized electrode. This procedure is open to the criticism that an IR drop through the solution will be included in the measurement unless the tip is placed against the electrode surface; and, if this is done, the capillary shields the electrode causing decreased current density, hence decreased polarization, at the important portion of the surface facing the tip. In addition, where the electrode reaction produces a film of appreciable resistance over the electrode, the direct method does not separate out the ohmic potential across the film (although in some cases it is preferable to consider this potential part of the polarization voltage).

2. Commutator method: The polarizing current is interrupted periodically and the measurement is made during the open-circuit intervals. In this way all ohmic potentials are eliminated. This method is complicated by the fact that the electrode potential must be measured at rapid intervals after opening the circuit, and the potential-time curve extrapolated to zero time. When the polarization is large it decays so quickly that the extrapolation becomes indefinite. Furthermore with interrupted current the polarization may fail to reach the desired continuous-current value.

3. Polarization-decay method: After the electrode has been polarized with continuous current for a

[1] Manuscript received February 26, 1952. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952. The author has kindly consented to a delay in publication so that this paper may appear in the special Theoretical Electrochemistry Issue.

[2] Detailed reviews of this subject have been presented by Ferguson (3) and Bockris (4).

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given time, the circuit is opened and the initial potential-decay curve recorded by means of an oscillograph. At low current densities any *IR* drop included in the decay curve is readily spotted and eliminated; at high current densities the initial polarization decay becomes too rapid to differentiate it from an *IR* drop with present equipment.

Thus each of the three methods has its limitations. The direct method is by far the simplest, consequently it is desirable to develop this one to high precision. Considerable work along this line has been done by Ferguson and coworkers (3, 5, 6), who studied the inclusion of *IR* drops by means of potential-decay curves; no *IR* drops were detected in measurements on a large number (but relatively

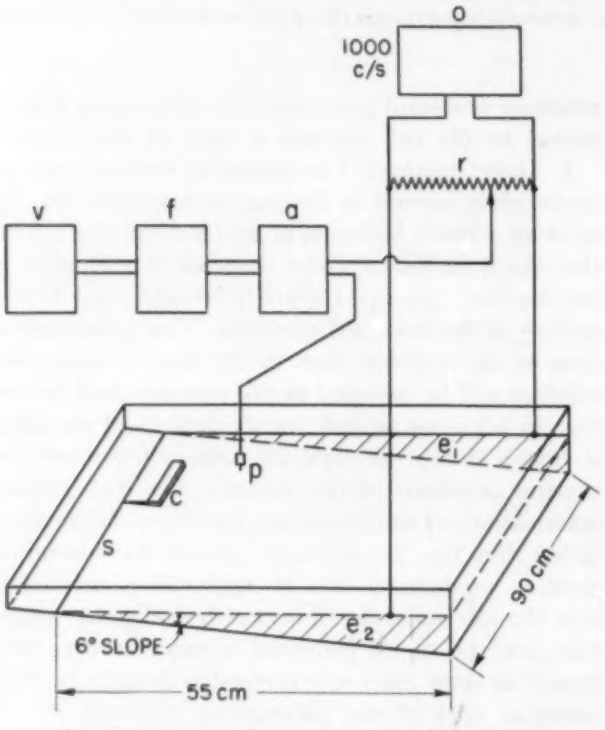

FIG. 1. Apparatus for measuring equipotentials

narrow field) of electrode systems. A more fundamental approach to the problem is the mapping of equipotential surfaces around the electrode and the capillary tip in order to determine both the ohmic potentials and the effect of shielding. Piontelli and Bianchi (7) have obtained such maps but used an incorrect model. Instead of a capillary tube, the model actually represented an infinitely long sheet of electrolyte between insulating plates. Nevertheless their results indicate that the shielding effect can cause serious error in polarization measurements.

In the present investigation, true models have been set up and the primary (electrostatic) distribution of equipotentials mapped out. The following systems were studied: (*a*) capillary in front of the electrode—the Luggin-Haber arrangement (8); (*b*) capillary behind a plane electrode having an insulated back—the arrangement used by Ferguson and Kleinheksel (6); (*c*) capillary through the back of the electrode and having its tip at the front surface—the arrangement favored by Piontelli (9).

Each of the capillary systems selected for study had an axis of symmetry passing through the middle of the capillary. It was sufficient, therefore, to trace the equipotential lines in any one plane containing the axis. Electrolytic models were set up in a wedge-shaped tank, and the equipotentials were mapped out in the plane represented by the top surface of the electrolyte.

PROCEDRRE

The potential-mapping apparatus, shown schematically in Fig. 1, was a modification of one described previously (10). A tank with a sloping bottom was filled with potassium dichromate solution up to the "shore line" *s*. The electrolyte represented a wedge sectioned from a conducting system having cylindrical symmetry. Thus the shore line was the axis of symmetry, and the copper electrodes e_1 and e_2 corresponded to two parallel disks inside a tube.

The insulator, *c*, which represented the wall of the capillary tube, had straight sides perpendicular to the top surface of the electrolyte, whereas the sides should be curved about the axis of symmetry. Little distortion was incurred, however, since the bottom of the tank sloped only 6 degrees. All insulators were sealed to the bottom of the tank with vacuum grease.

The electrical circuit was essentially an a-c Wheatstone bridge. A movable probe, *p*, dipping just below the surface of the electrolyte, was connected to the potentiometer, *r*, through a detector system *a-f-v*. The voltage across the detector was a minimum whenever the probe was on the equipotential line corresponding to the potentiometer setting. Thus equipotentials were readily traced out. The probe was carried by an accurate pantograph, by means of which the equipotential lines were mapped out on a drawing board near the tank.

The following improvements over the previous circuit (10) were incorporated in order to permit accurate potential measurements inside the capillary. Out-of-phase components were considerably increased in this high-resistance region. (*A*) The concentration of the potassium dichromate solution was increased tenfold (to 0.05%). Polarization at copper electrodes in this solution at 1000 cycles/sec, determined as previously described (10), was entirely negligible. (*B*) The oscillator, which had a shielded transformer at the output, was positioned 3 meters away from the bridge circuit. All connecting leads were either shielded or very short. (*C*) The out-of-balance signal from the bridge was first magnified

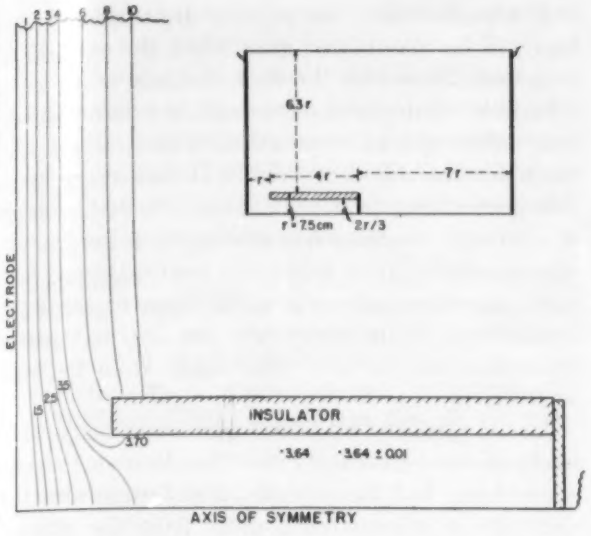

FIG. 2. Potential map, capillary of radius r at a distance r in front of the electrode.

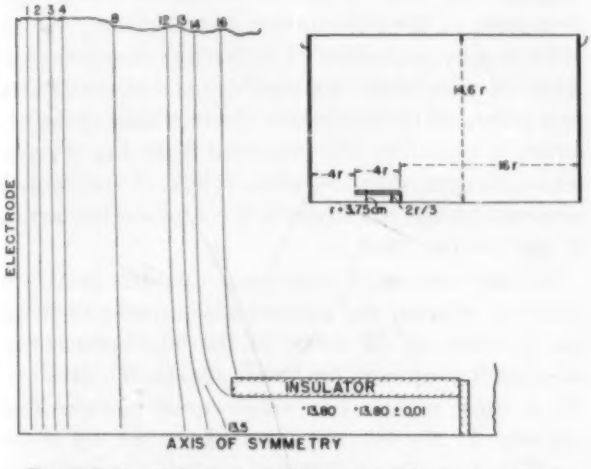

FIG. 3. Potential map, capillary of radius r at a distance $4r$ in front of the electrode.

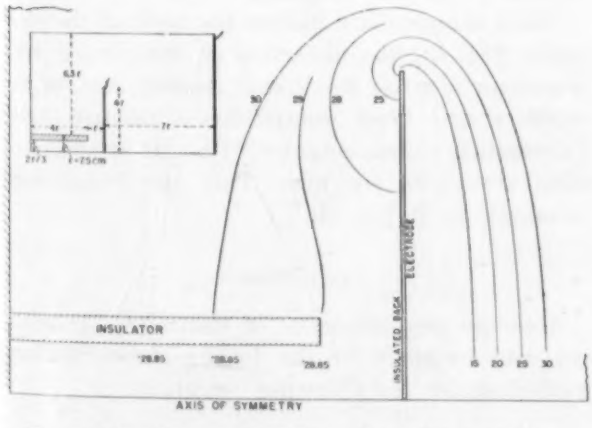

FIG. 4. Potential map, capilllary of radius r at a distance r from the insulated back of a finite electrode.

by a factor of 100 in the amplifier a (model 220, Ballantine Laboratories Inc.), then filtered through the 1000-cycle/sec band-pass filter f (type 830R, General Radio Company), and finally observed on a logarithmic-scale voltmeter (Ballantine model 300).

RESULTS

The models studied and their potential maps are shown in Fig. 2 to 5. The potentials of the lines and points shown are given as percentages of the total voltage across the two electrodes.

Fig. 2, 3, and 5 represent systems in which the current density over the electrode is uniform except

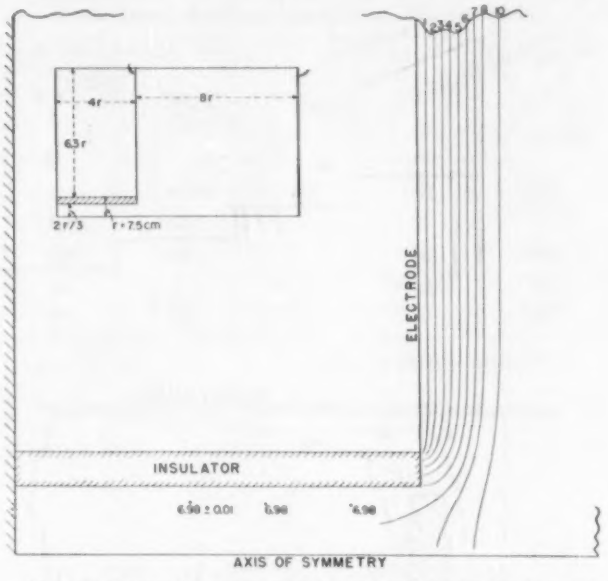

FIG. 5. Potential map, capillary through the back of the electrode and having its tip at the front surface.

TABLE I. *Normal potential gradients at the surface of the electrode*

Distance from axis of symmetry	Potential gradient, %/cm		
	Fig. 1	Fig. 2	Fig. 4
$r/2$	0.7	1.09	
r	0.9	1.09	
$3r/2$			1.9
$2r$			1.8
$3r$	1.17	1.10	1.69
$4r$	1.13	1.10	1.67
Theoretical*	1.11	1.11	1.67

* In absence of capillary.

for the distortion in the vicinity of the capillary. The degree of distortion is indicated by the data in Table I, which lists some measured potential gradients at the electrode. The normal gradient was determined from the curve of potential vs. distance from the electrode, by taking the slope at zero distance; the point on the curve representing the electrode position was obtained by extrapolation. The current density, i, is directly proportional to the normal gradient dV/dn, viz.,

$$i = -\kappa \, dV/dn$$

where κ is the conductivity of the electrolyte. The potential inside the capillary corresponds to the following distance from the electrode in the undistorted portion of the electric field: Fig. 2, 0.437 r; Fig. 3, 3.31 r; Fig. 5, 0.559 r; where r is the radius of the capillary.

Fig. 4 represents a case where the capillary is situated behind a finite electrode having an insulated back. The map shows clearly that a substantial ohmic drop exists between the capillary and the front surface of the electrode. This arrangement is basically unsatisfactory because the current density varies continuously over the surface of the electrode.

TABLE II. *IR drop* in mv between electrode and capillary tip of radius r = 0.03 cm separated a distance 4r*

i amp/cm² \ κ ohm⁻¹cm⁻¹	1	10^{-1}	10^{-2}	10^{-3}
10^{-1}	10	100	1000	
10^{-2}	1	10	100	1000
10^{-3}	10^{-1}	1	10	100
10^{-4}	10^{-2}	10^{-1}	1	10
10^{-5}	10^{-3}	10^{-2}	10^{-1}	1

* *IR* drop = 3.31 ri/κ v.

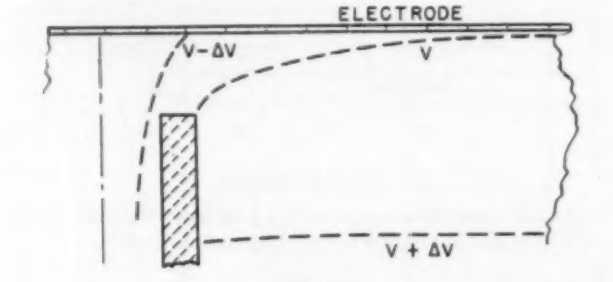

FIG. 6a

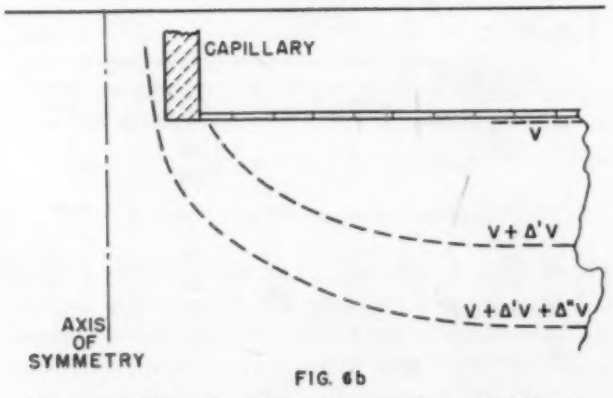

FIG. 6b

FIG. 6. Schematic potential maps for polarized electrodes.

Discussion

When the capillary tip is in front of the electrode and relatively far away (Fig. 3), it has little effect on the potential distribution at the electrode. As long as the current density remains the same all over the electrode, the primary potential distribution will be maintained even when the electrode is polarized. Thus with the tip a distance 4r (or more, if feasible) from a plane electrode, accurate polarization values can be obtained provided correction is made for the *IR* drop. Table II lists examples of these corrections for r = 0.03 cm. The usable ranges of solution conductivity and current density are approximately those below the heavy stepped line. Such corrections are only valid, however, when the conductivity of the electrolyte film next to the electrode does not deviate appreciably from the bulk conductivity.[3]

As the capillary tip is brought closer to the electrode, the current density over the electrode becomes nonuniform, and the potential distribution when the electrode is polarized will differ from the primary distribution. The distortion of the electric field reduces the current density at the electrode near the capillary tip (Fig. 2) and hence contributes a negative error to the polarization measurement. The *IR* error is always positive. Fig. 6a was drawn to illustrate the case where the capillary is sufficiently close to a polarized electrode that the resultant of the two errors is negative. The potential V in Fig. 6 represents the desired value, namely that in the solution adjacent to the electrode in the undistorted section of the electric field.

A large number of polarization studies have been reported wherein the authors attempted to prevent the inclusion of *IR* drops in the measurements by pressing the capillary tip firmly against the electrode. All of these polarization values must be considered too low. In the limiting case where the tip of the capillary forms a perfect seal against the surface of the electrode, the polarization would appear to be zero at all current densities.

When the capillary pierces the back of the electrode (Fig. 5), the distortion of the electric field causes an increase in current density next to the capillary and hence contributes a positive error. Polarization values obtained with this arrangement must always be too high. This case is indicated schematically in Fig. 6b.

Conclusions

Accurate measurements of electrolytic polarization can be made by the Luggin-Haber capillary method under the following conditions:

[3] Azzam and Bockris (11) used several capillary tips at various distances from the electrode, and extrapolated the results to zero distance. When correcting for *IR* drops by this means, it is important that the nearest tip be sufficiently far from the electrode so that no shielding occurs. The extrapolation will still be uncertain if a large conductivity change takes place between the electrode and the nearest tip.

1. The current density should be uniform over the electrode.

2. The capillary of radius r should be positioned at a distance of at least $4r$ in front of the electrode.

3. The IR drop included in the measurement should be evaluated and subtracted. At low current densities and in highly conducting solutions this correction can be made negligible.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. C. KASPER, *Trans. Electrochem. Soc.*, **77**, 353 (1940).
2. H. E. HARING, *Trans. Electrochem. Soc.*, **49**, 417 (1926).
3. A. L. FERGUSON, *Trans. Electrochem. Soc.*, **76**, 113 (1939).
4. J. O'M. BOCKRIS, *Chem. Revs.*, **43**, 525 (1948).
5. A. L. FERGUSON AND G. M. CHEN, *J. Phys. Chem.*, **36**, 1166, 2437 (1932); **38**, 1117 (1934); **39**, 191 (1935).
6. A. L. FERGUSON AND S. KLEINHEKSEL, *J. Phys. Chem.*, **42**, 171 (1938).
7. R. PIONTELLI AND G. BIANCHI, *Gazz. chim. ital.*, **80**, 581 (1950).
8. F. HABER, *Z. physik. Chem.*, **32**, 208 (1900).
9. R. PIONTELLI, *Z. Elektrochem.*, **55**, 128 (1951).
10. S. BARNARTT, *J. Electrochem. Soc.*, **98**, 311 (1951).
11. A. M. AZZAM AND J. O'M. BOCKRIS, *Nature*, **165**, 403 (1950).

Discussion Section

RESISTANCE OF TITANIUM TO SULFURIC AND HYDROCHLORIC ACIDS INHIBITED BY FERRIC AND CUPRIC IONS

Joseph R. Cobb and Herbert H. Uhlig (pp. 13–15)

R. D. Misch[1]: In regard to the blue film observed in the presence of inhibitor, it was suggested that occluded copper salts may be responsible. We have found in anodizing titanium in sulfuric acid solutions that thin oxide films exhibiting various interference colors are produced. The blue film mentioned in this paper may be of the same type, resulting from the oxidizing action of the inhibitors.

Herbert H. Uhlig: It is quite true, as Dr. Misch observes, that a blue film formed on titanium may represent an interference color and have nothing to do with occluded copper salts. During our corrosion tests, copper in solution gradually diasppeared, as determined by copper analyses, with the precipitated copper salts presumably entering the surface film formed on titanium. However, our later tests showed that blue films could form even before there was appreciable loss of copper so that in this case, the blue color was almost certainly not related to the color of copper salts and was, therefore, presumably an interference color.

M. E. Straumanis[2]: Bureau of Mines titanium becomes passive even in pure sulfuric acid[3]. The rate of corrosion in our experiments dropped almost to zero after a corrosion period of 80 to 400 hours. The bright surface of the metal (during the corrosion period) turned grayish violet when the passivation started. Remington Arms titanium covers itself with a layer of a similar color even in hydrofluoric acid when its concentration is below 0.2*N*. Thus, the formation of a protective film seems to be a property of titanium itself and does not depend on the presence of Cu^{++} and Fe^{+++} as inhibitors.

Did the authors observe the formation of a bluish film on titanium while dissolving in pure sulfuric acid (without the presence of inhibitors)? Maybe the inhibitors only stimulated the formation of the natural film?

What happened with the film when the samples were dried, and what with the adsorbed Cu^{++} and Fe^{+++}? Was the sample still passive after that?

Herbert H. Uhlig: We did not observe passivation of titanium by sulfuric acid after a long period of exposure, as reported by Dr. Straumanis, nor did we look for it. What we did observe is that in absence of cupric or ferric ions, the initial corrosion rate is extremely high in both boiling sulfuric and hydrochloric acids. Although there is a possibility that inhibitors stimulate the formation of a diffusion-barrier protective film, we observed no evidence for this. For example, we were able to activate titanium samples covered by a blue corrosion product film in hot hydrochloric acid accompanied by visible hydrogen evolution, yet without disappearance of the blue color until the reaction had proceeded for some time. The protective film, therefore, presumably underlies the thicker blue layer. Samples dried in the air were passive on re-exposure to boiling acids, but only temporarily so unless inhibitor was present.

This Discussion Section includes discussion of papers appearing in the Journal of The Electrochemical Society, **99**, No. 1–6 (January–June 1952).

[1] Argonne National Laboratory, Chicago, Ill.

[2] University of Missouri, School of Mines, Department of Metallurgy, Rolla, Mo.

[3] M. E. Straumanis and P. C. Chen, *Corrosion*, **7**, 229, Fig. 2, 3, 4, 5, 8, and 9 (1951).

THE ELECTRODEPOSITION OF COBALT-TUNGSTEN-MOLYBDENUM ALLOYS FROM AQUEOUS CITRATE SOLUTIONS

R. F. McElwee and M. L. Holt (pp. 48–52)

William Blum[4]: I wish to make a plea for more use of the equivalents in planning and reporting experiments in electrodeposition, also of reporting the composition of alloy deposits in "atomic per cents." Only through such data may we hope to throw light on the mechanism of electrodeposition, especially alloy deposition.

THE EFFECT OF INDIUM SULFATE IN CHROMIUM PLATING BATHS

Norman Hackerman and Tyleen Jensen (pp. 60–63)

G. E. Gardam[5]: It is a notable observation that easily deposited cations, such as copper, when added to a chromium plating bath, are not found in appreciable quantities in the deposit. It has also been found that addition of trivalent ions, such as chromium itself, iron, or aluminum appreciably increase the efficiency of deposition[6]. This has been used as a basis of a method increasing the efficiency of chromium deposition at high temperatures where the deposit is relatively soft (and incidentally crack-free) to provide a practical method of obtaining a machinable chromium deposit. A typical solution for this purpose contains CrO_3 250 g/l, H_2SO_4 2.5 g/l, and iron (added as ferrous carbonate) 25 g/l and is operated at 85°C, 200 amp/ft^2 (20.0 amp/dm^2) when the efficiency is 10 per cent and the hardness 444 DPN. A similar solution with lower CrO_3/H_2SO_4 ratio can also be operated.

It was suggested by the writer that, following Kasper's theory of chromium deposition[7], the added trivalent ions vary the permeability of the cathode film by being precipitated as their hydroxides on the colloidal chromium dichromate, whereby the acidity of the catholyte between the film and the cathode is slightly reduced and hydrogen

[4] National Bureau of Standards, Washington, D. C.

[5] Design and Research Centre for the Gold, Silver and Jewellery Industries, Goldsmiths' Hall, Foster Lane, Cheapside, E. C. 2, London.

[6] *J. Electrodepositors' Tech. Soc.*, **20**, 69 (1945).

[7] *Bur. Standards J. Research*, **9**, 353 (1932).

evolution made somewhat more difficult. It is now suggested that a similar mechanism may operate with trivalent indium.

NORMAN HACKERMAN: This could account for the current efficiency, although with indium there was no appreciable increase of current efficiency. The idea that it may act as a buffering constituent is wholly appropriate and should be capable of proof. However, it does not suggest reasons for the crack-free nature and bendability of the plate formed at 40°C. We have speculated on a mechanism which is regulatory in a similar sense. If the function of the sulfuric acid is to supply sulfate ions which vie competitively with chromate ions for the metal surface, then the sulfate ion/chromate ion ratio found empirically is a function of this competition. The latter, however, depends on the activity of the sulfate ions, and it may be that the In^{+++} by virtue of complexing sulfate ions acts as a means of more precise regulation of the activity, i.e., a "vernier" to provide more nearly the ratio needed to permit reduction of adsorbed chromate ions[8] more slowly and more uniformly in the plane of the electrode surface.

PRODUCTION OF TITANIUM INGOTS BY MELTING SPONGE METAL IN SMALL INERT-ATMOSPHERE ARC FURNACES

W. E. Kuhn (pp. 89–96)

L. W. EASTWOOD[9]: What is the melting efficiency when one pound of Ti is melted in an arc furnace by using 1 kwhr of power?

W. E. KUHN: Before replying to the discussion the author would like to thank the various contributors for the interest in his paper.

In answer to the question of Mr. Eastwood regarding melting efficiency, on the basis of a reported value of 384 calories required to heat and melt one gram of titanium, a value of 1.74×10^5 gram calories has been calculated for the energy required to heat and melt one pound of titanium. If this is done in one hour with a power input of one kilowatt, the total energy required will have been 1 kwhr or 8.6×10^5 gram calories. On this basis, the observed efficiency would be 1.74/8.6 or approximately 20 per cent.

G. R. FINLAY[10]: Is there any danger of melting through the copper crucible? If so, what happens?

W. E. KUHN: Concerning Dr. Finlay's question of the danger of melting through the copper crucible, the answer is yes, there is a danger of melting through the copper crucible, particularly when sponge exhibiting a high degree of spatter is being melted. When the arc penetrates the crucible wall and the least amount of water enters the crucible, the arc voltage immediately rises and the arc is extinguished. So long as the hole produced is very small (as is generally the case) and the flow of water into the furnace correspondingly small, there is little danger of an explosion.

[8] Reference (8) of the paper.
[9] Battelle Memorial Institute, Columbus, Ohio.
[10] Norton Company, Chippawa, Ontario, Canada.

C. H. CHILTON[11]: What gas was used to provide the inert atmosphere?

W. E. FEW[12]: Do you use *tank* argon, and is it used at atmospheric pressure?

W. E. KUHN: Tank argon of special purity (about 99.95 per cent) was used at atmospheric pressure, and this, I believe, answers the questions of Messrs. Chilton and Few.

DEVELOPMENT OF GRAPHITE ELECTRODES AND STUDY OF HEAT LOSSES WITH DIFFERENT ELECTRODES IN THE SINGLE ELECTRODE INERT-ATMOSPHERE ARC FURNACE

W. E. Kuhn (pp. 97–108)

S. A. PRUSSIN AND J. G. KURA[13]: We wish to congratulate the author on his excellent contribution to the understanding of arc furnace design. Particularly interesting are his calculations which show that under favorable arc conditions as much as 70 per cent of the heat energy passes through the ingot. We would like to point out that the efficiency, in terms of the energy required to heat the titanium metal from room temperature to its melting point and to melt it, is a much smaller percentage.

The data of Raeger, Rosenbohm, and Fonteyne[14] give a value of 384 cal/g for the heat energy required to heat and melt titanium. In Table VIII the author gives the working amperage and voltage, together with the corresponding values of melting time and charge weight. This permits the calculation of the actual energy used to melt a unit weight of titanium metal. Using the mid point in the ranges of the values given by the author, we obtain values of 5420, 7990, and 6550 cal/g utilized to melt the heats listed. On the basis that 384 cal/g are required to heat and melt titanium, the melting efficiency for the three heats in the order they are listed in Table VIII is 7.1, 4.8, and 5.9 per cent, respectively. Thus, although up to 70 per cent of the supplied heat energy enters the ingot, only 5 to 7 per cent of the total energy supplied is utilized in actual melting.

W. E. KUHN: The author first wishes to thank the various contributors to this discussion for the consideration given to his paper.

Although the author is not clear as to how Messrs. Prussin and Kura calculated their efficiencies, since neither melting time nor ingot weight was given in Table VIII, he is in agreement with the order of their values. A sample calculation for the six-pound ingot described on page 102 of the paper under discussion is summarized in Table I. An actual over-all efficiency of 3.2 per cent was calculated. If it is assumed that approximately 50 per cent of the energy enters the ingot (see Table VIII) and is considered useful because it does so, then the efficiency in terms of this useful energy is about 6.4 per cent.

It will be apparent that these efficiencies may be greatly varied by employing different design features. Thus for example, shorter arc lengths and greater electrode-to-cru-

[11] McGraw-Hill Publishing Company, Inc., New York, N. Y.
[12] Battelle Memorial Institute, Columbus, Ohio.
[13] Battelle Memorial Institute, Columbus, Ohio.
[14] *Rec. trav. chim.*, **55**, 615 (1936).

cible diameter ratio, which are made possible by using consumable electrodes, would be expected to further increase the effectiveness of the power.

P. H. BRACE[15]: From the block diagrams presented by the author, I gained the impression that there was appreciable carbon pick-up even with the tungsten electrode and that the highest hardness was shown by tungsten-electrode melts. What was the origin of the carbon in those cases?

W. E. KUHN: In reply to the question by Dr. Brace, the presence of the carbon is believed to result from the reduction of small amounts of phosgene in the $TiCl_4$ used to produce the sponge metal.

L. W. EASTWOOD[16]: Have you had any experience with tungsten electrodes containing thoria or rare earth oxides?

W. E. KUHN: The answer to the question of Dr. Eastwood is that we have not used tungsten treated with thoria or rare earth oxides. However, it has been reported that thoriated tungsten produces considerably more stable arcs of higher current density for melting titanium than untreated tungsten[17]. Also, one might expect similar results from additions of the rare earth oxides to tungsten electrode material.

TABLE I. *Sample calculation of melting efficiency for a 6-lb titanium ingot melted in a 3-inch diameter crucible using an electrode provided with a titanium-coated tip*

Weight of ingot lbs	Melting rate lbs/hr	Avg current amp	Avg voltage v	Power input kwhr	Theoretical calories to heat and melt 1 g titanium	Actual calories used to melt 1 g titanium	Efficiency %
6.25	3.6	925	25	23.1	384	12,170	3.2

THE RELATIONSHIP OF ALPHA AND BETA SILICON CARBIDE

Henry N. Baumann, Jr. (pp. 109–114)

J. H. WESTBROOK[18]: Please elaborate on the experiments on the formation of SiC in lead-silicon alloys, particularly with regard to the size, shape, and distribution of SiC particles formed.

HENRY N. BAUMAN, JR.: In all our experiments in which the object was to form silicon carbide by the reaction of the silicon from low melting alloys with carbon, the silicon carbide that was recovered was very fine. It consisted of either microcrystalline greenish particles that were isotropic when examined petrographically, or of greenish gray aggregates made up of particles so fine that the aggregate appeared opaque. It was necessary to chemically remove the residual alloy metals to obtain material that could be satisfactorily examined. The positive identification of beta silicon carbide was by x-ray diffraction.

The lead silicon alloy actually gave very little silicon carbide. A much more satisfactory experiment for illustrating this reaction was obtained when we used a silicon-aluminum-zinc alloy[19].

THE SYNTHESIS, FABRICATION, AND PROPERTIES OF BERYLLIUM CARBIDE

John H. Coobs and Walter J. Koshuba (pp. 115–120)

GUY FETTERLEY[20]: What type of mill is used for the preparation of Be_2C powder for hot-pressing? Can any liquid grinding medium be used? When steel balls are used for grinding, how much Fe is introduced? Can it be removed, possibly by carbonyl formation?

JOHN H. COOBS: As explained in the original paper, a four-quart, rubber-lined mill with steel balls was used for the grinding operation. About 1.5 per cent iron was introduced in this process.

Several liquids were tried as grinding media, for instance, carbon tetrachloride and kerosene. However, since Be_2C hydrolyzes slowly in the presence of water, any liquid medium must be very dry. Also, we found that the increase in grinding efficiency through the use of liquid media was more than offset by the tedious and time consuming separation of the Be_2C powder after grinding. The use of liquid media was thus discontinued.

No attempt was made to remove the iron introduced in the grinding process. It is quite possible that it might be removed by the carbonyl process. However, more recent developments have produced a finely divided Be_2C powder of high quality by direct synthesis, thus eliminating the need for extensive grinding operations.

JULIUS J. HARWOOD[21]: Are any special safety precautions necessary in the processing or handling of beryllium carbide?

JOHN H. COOBS: The usual precautions for handling of all beryllium compounds were observed. Specially designed, high-velocity exhaust hoods were used for all operations involving handling of powders or machining of specimens from hot-pressed bodies. Continuous air samples were taken and a working level of less than one microgram/cm^3 of beryllium was required before the hoods were approved for use.

THE MECHANISM OF THE CATHODIC HYDROGEN EVOLUTION REACTION

J. O'M. Bockris and E. C. Potter (pp. 169–186)

M. E. STRAUMANIS[22]: Cannot the breaks on the overvoltage-log current density curves be explained by changes in the surface of the cathodes during the electrolysis? It is very well known that the overvoltage rises if the electrolysis is continued sufficiently long at a constant current density and that the changes in the cathodic surface are accompanied by overvoltage changes.

What is the reproducibility of the breaks? Can the breaks be reproduced in both cases of increasing and decreasing current?

[15] Westinghouse Research Laboratories, East Pittsburgh, Pa.

[16] Battelle Memorial Institute, Columbus, Ohio.

[17] Round-Table Discussion, "Methods of Refractory Metal Melting," Spring Meeting, The Electrochemical Society, May 8, 1952.

[18] General Electric Company, Research Laboratory, The Knolls, Schenectady, N. Y.

[19] *J. Electrochem. Soc.*, **99**, 111 (1952).

[20] Box 26, Chippawa, Ontario, Canada.

[21] Office of Naval Research, Navy Department, Washington, D. C.

[22] University of Missouri, School of Mines, Department of Metallurgy, Rolla, Mo.

J. O'M. Bockris and E. C. Potter: Sharp breaks in the Tafel lines during cathodic hydrogen evolution on metals have been observed on smooth Pt[23] and Ag electrodes[24]. It is improbable that these breaks are due to changes in the surface of the cathode during electrolysis because (*a*) the breaks are usually accompanied by a sharp change in slope of the Tafel lines from, e.g., 0.03 to 0.12 approximately, these values being associated with definite mechanisms of the hydrogen evolution reaction; (*b*) changes occur at definite potentials, which would seem unlikely if change on electrode surface were the cause. If the changes were due to changes in the type of surface (such as its "activity," or heat of adsorption of hydrogen atoms) one might expect a more gradual change in the Tafel line, e.g., a shifting up or down corresponding to a new i_0 value.

The "well known" changes with time to which Professor Straumanis refers are probably caused (in many cases in the older work at least) by the continued deposition and/or adsorption of impurities on the electrode surface which take place during electrolysis. These changes can be shown to disappear if the solution is sufficiently well purified, as by pre-electrolysis[25]; in these specially purified systems there is no change with time for many metals. For metals which easily adsorb hydrogen (e.g., Ni) there is a brief and steady reproducible change with time at the beginning of the electrolysis, and then the overpotential remains indefinitely constant.

The reproducibility of the breaks in the case of Bockris and Azzam's work on Pt was only fair (±10–15 mv). In Bockris and Conway's work it was about ±5 mv. In the latter work the breaks could be reproduced with ascending and descending currents. In the former a hysteresis phenomenon was observed. One would suspect this as being due to the presence of impurities, although increased preelectrolytic purification failed to bring about alteration in the phenomenon.

REMOVAL OF EMBRITTLING GASES FROM ZIRCONIUM

W. C. Lilliendahl, E. D. Gregory, and D. M. Wroughton
(pp. 187–190)

J. H. Westbrook[26]: To what extent does oxygen dissolve in solid zirconium metal?

W. C. Lilliendahl: The solubility of oxygen in zirconium has been reported by J. D. Fast to be approximately 40 atomic per cent. (*Philips Tech. Rev.* **3** No. 12, Dec. 1938).

Arthur D. Beard[27]: Can you comment on treatment of other metals?

W. C. Lilliendahl: Oxygen should be removed from all metals whose oxides are reduced by metallic calcium, and where the mobility of oxygen in the metal is a finite value at the permissible temperature of soak. This temperature would be in some cases limited by the tendency of calcium to alloy with the metal under treatment.

The process has been applied successfully to zirconium, titanium, and vanadium.

L. W. Eastwood[28]: (1) What is the maximum thickness of specimens that can be deoxidized on a practical basis?

(2) What hardness and oxygen gradients exist in such deoxidized thick specimens?

(3) What is the hardness of the low oxygen specimen listed in Table II?

W. C. Lilliendahl: (1) The rate of oxygen removal as a function of thickness of the treated metal has not been determined. The rate of diffusion of oxygen in zirconium at 1000°C or higher suggests that thick sections could be treated on a practical basis.

(2) Our data are limited to 0.128-in. diameter rod. The measurements would not detect a gradient in the treated pieces as the oxygen content is approaching the limit of the analytical method.

(3) The figures in Table II are calculated values and do not represent actual material as stated in the paper.

ARC MELTING OF ZIRCONIUM METAL

H. L. Gilbert, W. A. Aschoff, and W. E. Brennan, II
(pp. 191–193)

L. W. Eastwood[29]: (1) Have alloys been made by using the consumable electrode? If so, how uniform is their composition?

(2) What are the possibilities of making the consumable electrode continuously in the furnace or in an apparatus attached to the furnace?

H. L. Gilbert: (1) In regard to the question of alloy production by consumable electrode we have produced several with good results. Specifically, a one per cent tantalum alloy was produced by putting tantalum wire in the briquets used to make up the electrodes. Samples taken throughout the ingot varied from 0.90 to 1.14 per cent tantalum.

(2) Concerning the fabrication of continuous electrode within the furnace, we consider the joining of prefabricated sections or pressed bars or briquets to be the most promising possibility. These prepared compacts would be joined by butt welding, high-frequency sintering or arc welding as melting progressed.

John G. Kura[30]: What method is used to obtain the seal around the starting plug?

Is the arc length critical for efficient operation?

What control factors are available for overcoming unsoundness in the ingot, if unsoundness is a problem?

H. L. Gilbert: No seal is necessary around the starting plug as the entire furnace is filled with inert gas.

Arc length during melting operations is controlled to a major extent by a choice of gas mixture employed. About 80 per cent helium, 20 per cent argon permits operation with reasonable voltage drop across the arc but without

[23] Bockris and Azzam, *Trans. Faraday Soc.*, **48**, 145 (1952).
[24] Bockris and Conway, *ibid.*, **48**, 724 (1952).
[25] Bockris and Conway, *Trans. Faraday Soc.*, **45**, 989 (1949).
[26] General Electric Company, Research Laboratory, The Knolls, Schenectady, N. Y.
[27] General Electric Company, Research Laboratory, The Knolls, Schenectady, N. Y.
[28] Battelle Memorial Institute, Columbus, Ohio.
[29] Battelle Memorial Institute, Columbus, Ohio.
[30] Battelle Memorial Institute, Columbus, Ohio.

undue thermal loss to the walls. A long arc in pure argon is not effective for satisfactory melting.

Usual difficulties with ingot unsoundness involve the area of the interruption caused by changing electrodes. No control of this is considered possible short of going to a continuous type electrode.

EFFECTS OF WORKING ON THE PROPERTIES OF MOLYBDENUM

E. S. Byron and R. F. Baker (pp. 194–196)

ROBERT M. PARKE[21]: How do you explain the low ductility in the thickness direction?

E. S. BYRON: Our experiments to date have given us no explanation of this.

SOME FACTORS IN ANODIC PROCESSES ON CORRODING METALS

T. P. Hoar and U. R. Evans (pp. 212–218)

NORMAN HACKERMAN[22]: In connection with studies on the corrosion of steel by air-free aqueous solutions of fatty acids and carbon dioxide, we have found that the initial reaction rate had a determining influence on the subsequent rate. It has been possible to relate this effect to the nature of the initially precipitated corrosion products, not so much with respect to measureable chemical composition, but rather with respect to its physical form. We are now attempting to show that the continuing corrosion rate is dependent on the defect nature of the corrosion products and that this in turn is a function of the way the solid precipitated, e.g., on the rate of nucleation.

T. P. HOAR AND U. R. EVANS: We are interested in Professor Hackerman's approach to the problem of the part played by early corrosion products in determining the subsequent rate of corrosion. Other cases of the phenomenon, as well as the interesting one he mentions, are known, especially in the field of atmospheric corrosion; we believe the application of defect structure theory now being made by Professor Hackerman may well be extremely fruitful.

A HYDRIDE BATH FOR THE ELECTRODEPOSITION OF ALUMINUM

Dwight E. Couch and Abner Brenner (pp. 234–244)

R. SCOTT MODJESKA[23]: (1) What current densities were employed? (2) What voltages? (3) What temperatures?

DWIGHT E. COUCH: The following answers are given to the queries of Mr. Modjeska: (1) 1–4 amp/dm^2; (2) 12–15 volts; (3) room temperature. Higher temperatures were investigated but deposits were not as good and solution decomposition took place.

JOHN F. GALL[24]: (1) What anode compositions have you tried? (2) What was the anode current efficiency?

ABNER BRENNER: (1) We have used anodes only of pure aluminum and 2S aluminum, and (2) they dissolve with 100 per cent current efficiency.

DENNIS R. TURNER[25]: (1) Have other alkali hydrides been used in place of lithium hydride and, if so, with what success?

(2) Are the constituents of the plating bath present in saturated quantities?

ABNER BRENNER: (1) Sodium hydride and calcium hydride were tried without success. Aluminum hydride may be used in place of lithium hydride but this substitution is not feasible because the hydride must be made from lithium-aluminum hydride.

(2) The plating bath is not saturated with respect to aluminum chloride or lithium hydride. The concentration of aluminum chloride may go as high as 5*M*. The bath will dissolve lithium hydride to the extent of about 1.5*M* but will give aluminum deposits successfully with concentrations of only 0.5*M*.

PASSIVITY OF IRON IN NITRIC ACID

Harry C. Gatos and Herbert H. Uhlig (pp. 250–258)

EARL A. GULBRANSEN[26]: The very interesting experiments by Gatos and Uhlig emphasizing the adsorption theory of passivity should stimulate many others holding other views to restate their ideas in terms of modern concepts. I should like first to make two comments concerning the paper itself and later a general comment on the oxide theory of passivity.

I would like to second Dr. Cohen's suggestion that the effective passive films are formed slowly by exposure of new metal surfaces to air. We have noted this in the formation of a chemisorbed film of oxygen on pure graphite at room temperature. It may be worth while to check this point with your sensitive method.

Next, I would like to emphasize the point that the reaction of iron in a HNO_3 environment is a rate process and that reaction is still occurring under so-called passive conditions. It would be well to obtain quantitative values for these reaction rates so that different surfaces and conditions can be compared.

Finally, I would like to comment on some suggestions made to me by Dr. Verwey of the Philips Laboratories in Eindhoven, Holland. These suggestions give support to the oxide film concept of passivity and provide a mechanism for the breakdown of oxide films due to the influence of certain ions, e.g., chloride and fluoride ions. Verwey has shown that if Li^{I} ion is substituted in NiO, some of the Ni^{II} ions are changed to Ni^{III} ions to conserve neutrality. This greatly affects the conductivity of the oxide. Ten atom per cent of lithium changes the conductivity by a factor of a million. The process of solid solution of one ion into another oxide leads to a mechanism of controlled valency of the semiconductor. Similarly, the anion may be substituted. Thus, if a small amount of chloride ion could substitute for the oxygen ion in nickel oxide, some of the

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[22] Department of Chemistry, University of Texas, Austin, Texas.

[23] 600 Blue Island Avenue, Chicago, Ill.

[24] Pennsylvania Salt Manufacturing Company, Philadelphia, Pa.

[25] Electroplating Projects Laboratory, Westinghouse Electric Corporation, East Pittsburgh, Pa. *Present address*, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

[26] Westinghouse Research Laboratories, East Pittsburgh, Pa.

oxygen ions would have to take on a minus three charge. This provides a simple mechanism for changing the conductivity of the film. Its electrode potential would change, corrosion could occur at a higher rate, and the metal would no longer be called passive. Although Goldschmidt's values for the ionic radii show that the chloride ion has a larger ionic radius than the doubly charged oxygen ion, other tables give values somewhat closer in agreement.

HERBERT H. UHLIG: Dr. Gulbransen's observations that passive films are formed slowly on new metal surfaces is in accord with our more recent observations not yet published (Montreal Meeting) on the progress of passivity in 18-8 stainless steel exposed to aerated water as measured by oxygen take-up by acid-pickled metal. Here, the initial rate of passivation is very rapid—faster than we can measure within a few minutes—but in the latter stages, the passivation can be called slow. In the passivation of iron by nitric acid, the initial rate of reaction is very high before passivity is established. Some time during this initial reaction, the metal quite suddenly becomes passive, whereupon the rate thereafter is low. Quantitative data on the low rate for passive iron are given in our paper, but measurements of the fast rate have not yet been attempted. We only know that it is properly termed a rapid reaction, and that perhaps the rate is on par with the rate of reaction of iron with dilute nitric acid.

The suggestion of Dr. Gulbransen, quoting Dr. Verwey, is an interesting possibility. It seems to me that this mechanism, as others have shown, almost certainly applies to factors affecting tarnish and high temperature oxidation where diffusion of ions through a reaction-product layer is the rate-controlling mechanism. It is well established that trace quantities of various contaminants on the surface of a metal or in the gas phase (e.g., sulfur) can affect the rate of high temperature attack. Perhaps Dr. Gulbransen's suggestion regarding chloride ion may explain some results we obtained showing that a trace of sodium chloride on the surface of a 5 per cent chromium steel accelerates oxidation in air at 900°C by a factor of 2.5[37].

Hoar and Evans[38] have proposed that a mechanism similar to that of high temperature corrosion may also apply to aqueous corrosion reactions, a proposal apparently closely related to that which Dr. Gulbransen suggests here. This assumes a reaction product film to be the basic seat of passivity.

In our previous discussions of the effect of chloride ions in breaking down passivity, we have considered the chloride ion as competing with passivators like oxygen or chromate ion for a place on the metal surface, with the metal as adsorbent and the passivator or chloride ion as the adsorbate[39]. In this picture, passivity is assumed as being produced by adsorption, particularly chemisorption, on the metal surface because of the high affinity of the metal for the passivator, accompanied by a high activation energy for reaction (the reaction to form a stoichiometric compound is slow). Chlorides and fluorides also have high affinity for the metal, but the activation energy for reaction is either small or zero; hence, if either of these two substances succeeds in displacing a passivator from the metal surface, they react immediately to form soluble salts, a process which automatically destroys passivity (or they may form a corrosion product layer such as silver chloride on silver, where they produce passivity through the quite different mechanism of a protective diffusion-barrier layer). Halogen ions, therefore, because of rapid reaction with the metal, do not *produce* but destroy passivity, whereas chromates on iron, or oxygen or carbon monoxide on stainless steels react only slowly and produce passivity primarily by means of an adsorbed film. In the latter instances, and especially in these cases, the chemical affinities of the metal surface are in part satisfied by the strong bonding of the chemisorbed layer with the metal surface, this, in turn, accounting for the chemically unreactive or passive surface.

Since the transformation of an adsorbed film into a corrosion product layer is bound to occur in time, even though this is slow, the mechanism of growth of the reaction product can well follow, and probably does in many instances, the mechanism proposed first by Wagner for high temperature or tarnish films, and now by Hoar and Evans, and Gulbransen for reaction-product films in aqueous environments.

[37] A. BRASUNAS AND H. H. UHLIG, *ASTM Bull., No. 182*, p. 71, May (1952).

[38] *J. Electrochem. Soc.*, **99**, 212 (1952).

[39] B. KABANOV, R. BURSTEIN, AND A. FRUMKIN, *Disc. Faraday Soc.*, No. 1, p. 268 (1947).

THE INFLUENCE OF INHIBITORS ON THE DISSOLUTION OF IRON IN ACID SOLUTION

J. Elze and H. Fischer (pp. 259–266)

J. O'M. BOCKRIS[40]: Bockris and Conway[41] found a parallelism between the degree of effectiveness of the inhibitor and the increase in hydrogen overpotential found in the presence of such inhibitors. This parallelism appears to mean that the inhibitors work by reduction of the velocity of hydrogen evolution (probably by reduction of the heat of adsorption of hydrogen on the surface). This view is in agreement with Fischer and Elze, who found that the inhibitors only slightly change the metal dissolution overpotential and that they are effective for iron only if the hydrogen atom combination reaction occurs.

H. W. SALZBERG[42]: Dr. Bockris has stated that, in the inhibition of corrosion of iron, the fact that the inhibitor raises the overvoltage indicates the role of the inhibitor is not merely that of mechanical surface blockage. However, adsorption of inhibitor at active centers for combination will decrease the combination rate and thus increase the concentration of atomic hydrogen. This will increase the overvoltage, as found by Elze and Fischer. Therefore, development of overvoltage does not preclude inhibition by mechanical means alone.

NORMAN HACKERMAN[43]: The authors say that the use of a thiourea did not provide inhibition and may even have increased the reaction rate. The thiourea was pre-

[40] Imperial College of Science, London, S. W. 7, England.

[41] *J. Phys. Chem.*, **53**, 527 (1949).

[42] Naval Research Laboratory, Washington, D. C.

[43] Department of Chemistry, University of Texas, Austin, Texas.

sumably added to the aqueous system in these experiments. Because of the very low solubility of these compounds in water, their ineffectiveness is not very surprising.

We have found that diethyl and dibutyl thioureas will adsorb on steel from benzene solution, in which they are somewhat more soluble. If steel coupons, treated by exposure to such benzene solutions, are thoroughly washed with benzene to remove all adhering and physically adsorbed thiourea and then exposed to aqueous 4*N* HCl, the rate of reaction is reduced to less than 20 per cent of that for an untreated coupon. This effect was generally rather long-lived, that is, of the order of days. This suggests that inhibitors might be placed on a metal surface out of contact with the corroding medium and be quite effective if the medium does not desorb or otherwise remove it from the metal surface.

T. P. Hoar[44]: With R. D. Holliday, I have investigated the mechanism of the action of several series of inhibitors, such as the substituted thioureas and substituted quinolines, on the dissolution of 0.1 per cent carbon steel in warm sulfuric acid. Confirming my previous results[45], we find that the addition of inhibitor nearly always makes the corrosion potential more noble (it is, however, made more basic by the addition of *small* amounts of the thioureas). This means that, under conditions of natural corrosion without applied current, these inhibitors usually affect the anodic process to a greater extent than the cathodic[46]. We have also obtained the true anodic and cathodic polarization curves in the neighborhood of the natural corrosion potential, by measuring the rate of metal dissolution and the applied anodic or cathodic current at a series of potentials[47], both for plain acid and inhibited acid. These show that the rate of the anodic process at any potential is nearly always more reduced by the inhibitor than that of the cathodic process—a fact also found by Elze and Fischer for Victoria blue and crystal violet; thus, the inhibitor acts more potently on the anodic than on the cathodic reaction. Under conditions of high cathodic polarization to potentials far more negative than those obtaining in natural corrosion, we find, in agreement with Elze and Fischer and also with Bockris and Conway[48], that the action of such inhibitors in slowing down the cathodic reaction becomes much more marked; this must mean that the inhibitor becomes more strongly adsorbed on centers otherwise active for the cathodic reaction, at very negative potentials. This result does *not* imply, however, that the action of inhibitors is mainly cathodic under the conditions of lower current density and more noble potential that obtain in natural corrosion.

[44] Department of Metallurgy, University of Cambridge, Cambridge, England

[45] T. P. Hoar, "Pittsburgh International Conference on Surface Reactions," p. 127, Corrosion Publishing Co., Pittsburgh (1948).

[46] T. P. Hoar, *Chimie et industrie*, **41**, 118 (1939).

[47] T. P. Hoar, *Trans. Electrochem. Soc.*, **76**, 157 (1939).

[48] J. O'M. Bockris and B. E. Conway, *J. Phys. Chem.*, **53**, 527 (1949).

Fiftieth Anniversary

THE CHARTER MEMBERS GREET THE SOCIETY

Upon the occasion of the Society's Golden Jubilee, we are fortunate to have messages of greeting from all of the living charter members. Arranged alphabetically, these letters follow:

Bel Air, Maryland
July 21, 1951

I am asked for an appropriate 'word' as one of the nine surviving charter members. My memory picture of the charter meeting is that of a group of very enthusiastic and relatively young men—I was 24 at the time—who had come to realize some of the scientific possibilities in the field lying between classical chemistry and physics and the scant sympathy for half-breeds in the existing technical societies.

Those early meetings were the most interesting society sessions I ever attended. We—I in particular—did not know too much of what we were talking about but papers and their authors were certainly kicked around and even when licking your wounds you knew you had learned something. Nowadays papers seem to get about as much audience attention as radio commercials.

Today if we should strictly eliminate electrical phenomena from all chemistry and physics there would be little left and where electronics will lead us man knoweth not. The electrical fringes where the two meet are still the most exciting fields of exploration.

So let us make the most of our catalytic heritage.

With kindest regards,

Sincerely,
LAWRENCE ADDICKS

Ithaca, New York
July 16, 1951

I don't know how accurate one's recollections are of things that happened fifty years ago. My impression is that the American Chemical Society then had membership requirements which would not be met by all of those who were interested in electrochemistry.

The Chemical Society would not change its rules so we had to start and did start an electrochemical society. Being crippled I cannot look this up myself; but it should be easy to verify this, though I admit that it now sounds improbable.

Yours sincerely,
WILDER D. BANCROFT

New Haven, Connecticut
September 20, 1951

As a charter member of the Electrochemical Society I wish to extend my most hearty greeting to every member of the Society.

My thanks and appreciation are expressed for the work done by all past and present officials who have made the Electrochemical Society such an outstanding organization.

Upon my retirement from teaching at Yale, I gave all of my volumes published by the Electrochemical Society to the library of the Sterling Chemical Laboratory of Yale University.

With very best wishes for future accomplishments, I am

Yours sincerely,
WALTER M. BRADLEY

Bloomington, Indiana
October 3, 1951

Greetings to fellow members of the Electrochemical Society, —the Society that has been and is the greatest force in building up our tremendous electrochemical industry of the United States.

The inspiration we received when we met at the meetings and became acquainted with such men as Joseph W. Richards, Edward Acheson, Dr. Haber of Germany, Hutton of England, Charles M. Hall, Elmer Sperry, the Taylors of New York, Burgess, Kalenberg, Bancroft, and many others, gave us the enthusiasm to go home and push hard our investigations in electrochemistry. The Society was and still is the main force for continued interest in the investigation and development of electrochemical processes, because it was and is a small group of persons who think alike.

I wish that the general public, the chemists and engineers of the U. S. A. were more familiar with the extent of the electrochemical industry. I deplore the fact that electrochemical subjects have been dropped from the curricula of many of our colleges and universities. No subject is more suitable for fundamental training in engineering and science. We should see that the courses in applied and theoretical electrochemistry be restored to the curricula of our universities and engineering schools. We should see that the universities turn out chemists and engineers who are well trained in applied electrochemistry.

Yours sincerely,
O. W. BROWN

Philadelphia, Pa.
August 3, 1951

Time, like space, is relative and infinite. In my memory I can span the period of fifty years since the founding of the American Electrochemical Society (1901–1951) in but the time it takes to dictate these words.

In accordance with my recollection, I was invited to become a charter member of the American Electrochemical Society by Dr. Carl Hering. The small group of Philadelphia founder members with whom I had contacts were the follow-

ing: Carl Hering, Charles Reed, Pedro Salom and Dr. Roeber.

If my recollection is not faulty, Dr. Roeber had but a short time prior to the organization of the Society migrated to America. Dr. Hering used him in some capacity in connection with his consulting practice. Other persons known to me at the time were the following: Acheson, Oldsbury, Tone, Horry and Fitzgerald.

It was through my acquaintance with Carl Hering that I became interested in the electrothermic field. Hering had discovered the "pinch" effect. Dr. Edwin F. Northrup (Acheson medallist) had explained the phenomenon and had developed the theory and the well-known formula for calculating pinch pressure.

Hering had an idea for utilizing the electromagnetic forces of the pinch phenomenon for operating an electric furnace. I had a metallurgical problem and believed that a furnace as conceived by Hering could be successfully used for conducting the metallurgical process I had in mind. I offered to spend a maximum of $500 to build a small equipment to demonstrate the practicality of Hering's idea. There is an old Chinese proverb, as follows: "No matter how long the journey the first step must be taken." The expenditure of this initial small amount was the first step that led to the establishment of four separate companies for the development and exploitation of electric furnaces; namely, Ajax Electric Furnace Corporation, Ajax Electrothermic Corporation, Ajax Electric Company, Inc. and Ajax Engineering Corporation.

Each one of these companies specializes in a different type of furnace, all using the electromagnetic circulation due to pinch pressure, coupled with other electromagnetic and thermal effects.

The expenditure of the initial $500 resulted merely in establishing the fact that there was merit in the idea of applying electromagnetic circulation. Hering proposed the use of electrodes. It required an expenditure of $40,000 to determine that the use of electrodes in this type of furnace (without going into detail) was impractical.

Success soon followed after discarding electrodes and utilizing the electromagnetic forces in an induction furnace. This type of furnace was soon demonstrated to be ideal as a brass melter. It was rapidly adopted by the wrought brass industry. Melting of brass in that industry actually underwent a revolution, in that all the old pit-crucible type furnaces were thrown out and this furnace substituted. Today practically all the metal melting in the brass mills of the world is done in induction furnaces of this type.

Necessity of maintaining a fairly large heel of metal (to complete the secondary circuit) restricted the use of this furnace very largely to 24-hour-a-day operation. With this in mind, I retained Dr. Northrup to study the possibility of devising an induction furnace that would not have this drawback. The well-known high frequency induction furnace resulted. Today there is a high frequency induction furnace industry. Since the patents have expired many concerns have entered the field. High frequency induction is used not only for melting but for heating solids, surface hardening, and for many other purposes.

The next project was to develop a furnace for melting and circulating molten salts. Such furnaces are extensively used for many heat treating processes (34 are listed in our catalog). I name but a few as follows: cyclic annealing, case hardening, isothermal heat treatment, martempering and heating billets for forging and extruding, etc. This type of furnace is not an induction furnace but uses electrodes, as originally contemplated by Hering. The use of electrodes in this type furnace is entirely practical. The circulation due to electromagnetic forces is of great magnitude.

The original induction furnace, largely used in the brass industry, was unsatisfactory for melting aluminum. When used for melting aluminum the secondary channels became rapidly clogged with aluminum oxide. In a furnace of modified design this difficulty has been entirely overcome and a furnace of this type is in very extensive use in the aluminum industry.

A company was organized to specialize in each of the fields enumerated: viz.,

(1) Submerged resistor induction furnace for melting brass and other metals.
(2) High frequency coreless induction furnace for many melting and heating applications.
(3) Salt bath furnace for heat treating and other applications.
(4) Submerged resistor induction furnace for aluminum melting.

Each company has spent large sums for research and development. The companies specializing in each of these fields have long been established and are well known. They are enumerated above.

Unfortunately, due to my having taken an active part in three other national societies; viz., American Institute of Metals, American Society for Testing Materials and American Foundrymen's Society, I did not have the time to take an active part in the affairs of the American Electrochemical Society. I have, however, kept in close touch with its splendid accomplishments through its publications. As one of the nine surviving charter members I extend to the officers and members of the Society my hearty congratulations upon the occasion of its 50th anniversary. I am sure the Society will continue its good work on an ever expanding scale.

Yours sincerely,
G. H. Clamer

Boulder, Colorado
August 8, 1951

Your letter of 8/1 has been received and I was much interested but find it somewhat difficult to reply after a lapse of nearly 50 years.

You are right, I retired—on account of age—from the Deanship of the College of Engineering, University of Colorado, to the status of Dean and Professor Emeritus, in November 1943. Since formal retirement I have been busy on various projects, some related to engineering and some to business.

I am very well and active.

In 1902 I was a member of the staff of the Department of Electrical Engineering at the University of Nebraska in Lincoln and in addition to other duties I set up a modest Electrochemical Laboratory and offered a short course in that subject. As I look back on it now, both the laboratory and the course were *very* modest but at that time they may have served a useful purpose.

As I remember it, my laboratory and classroom course dealt chiefly with primary and secondary batteries, the controlled deposition of metals, and some work on electric furnaces.

When I learned of the plan to found an Electrochemical Society, in 1902, it was only natural that I should wish to join with others of like interests.

I enjoyed and benefited from the publications and contacts afforded by the new Society until a change of position gradu-

ally made it necessary for me to devote my time and efforts to other fields of electrical engineering. I have never lost my interest, however, in electrochemistry.

In June of 1905 I went with the General Electric Company in Schenectady intending to return to Nebraska in the fall, but while there I was offered and accepted the headship of the Department of Electrical Engineering at the University of Colorado at Boulder. This position I retained for many years and was appointed Dean of the College of Engineering in 1919. I continued in that position until retirement as noted above.

My congratulations to the Society on its 50th anniversary and very best wishes for its continued usefulness.

Sincerely yours,
H. S. EVANS

Cambridge, England
31st July, 1951

I was most interested to receive your letter of July 16th and to be reminded that I am one of the nine surviving charter members.

With regard to the first meeting of the Society, fortunately my memory is very clear and I kept some detailed notes. I often enjoy reminiscing on this visit, which I specially planned in order to take part in the Niagara Falls meeting of the Society where I spent ten very happy days, September 11th to 20th, 1902. These were very young days for the electrochemical industries, and most of them were run rather secretly, but Professor Fritz Haber and I, as oversea visitors, were treated very generously and were shown round most of the works.

At this meeting the first issue of "Electrochemical Industry" was circulate. Amongst others who have become famous in the annals of the Society and outside it, I remember intimate talks with the following: Prof. J. W. Richards, C. J. Reed, Carl Hering, E. G. Acheson, Charles M. Hall, W. R. Whitney, Prof. W. D. Bancroft, C. F. Burgess, F. A. J. FitzGerald, F. M. Beckett, C. S. Bradley, F. J. Tone, E. R. Taylor, C. E. Acker.

My subsequent visits to America have impressed me, as they do most Europeans, with the wonderful tempo of advance and keen appreciation of the possibility of new technical developments which are so characteristic of your country, but those ten days spent at Niagara Falls in close contact with so many of your electrochemical pioneers are still red letter days in my memory.

With heartiest congratulations to the Society and its noble band of honorary officers,

Yours sincerely,
R. S. HUTTON

Lockport, New York
July 19, 1951

I have your communication of the 16th and, unfortunately, I am so occupied with my different jobs that I can't comply with your request. However, I am sending you under separate cover copy of my "Incidents by the Way" and if you will note the marked pages you will see the situation as it concerns my career. You may use as little or as much as you choose.

Yours very truly,
WM. R. KENAN, JR.

[From this autobiography, it appears that Mr. Kenan has led a most eventful life and has engaged in a wide variety of pursuits. He has, for example, held executive positions in banking, building construction, hotel, water, railway, land, farming, and power companies. He has established and contributed to many philanthropies. To quote his own words, "It is given to few men to experience the joy I have had in helping young people to complete their education, young students who might otherwise have faltered by the way through lack of funds, and few men whom I have known have had the satisfaction of honoring the name they bear through such cultural memorials as the Kenan Foundation, erected in the city of my birth; the Kenan Stadium built for my alma mater, the University of North Carolina, that has thrilled thousands of people by its beauty; Camp Kenan on the shore of Lake Ontario at Barker, New York, which has been such a happy medium for many of the youth. . . . And it has given me a lot of satisfaction to promote the varied interests carried on at Randleigh Farm where through scientific research and practical application we have been able to reveal new controls and methods otherwise impossible for the average farmer to obtain. . . ."

Mr. Kenan is a graduate of the University of North Carolina which fifty years after his graduation conferred on him the degree Doctor of Laws. While still a student at the University under Professor F. P. Venable, he undertook the examination of a dark colored material obtained by the Professor from a furnace in which T. L. Willson had been attempting to produce calcium. Young Kenan found that the gas evolved upon contact of this material with water was acetylene and thus that the furnace product contained not calcium but calcium carbide. A syndicate was formed in Philadelphia under the name of the Carbide Manufacturing Company to produce acetylene from calcium carbide and young Mr. Kenan, then 23 years old, was offered his first job with this concern. His duties as defined by the president of the company were described in these words: "In the event of your forming a connection with our company, you will have entire charge of the laboratory and the office at all times. We will expect you to work ten hours a day seven days a week. During six hours of this time, you will have charge of the plant and of all men at work at such time. During the rest of the ten hours, we will expect you to make tests of the carbide from each charge of the furnace and make an occasional determination of lime in the furnace mixtures. There will be also submitted to you for analysis samples of lime and coke. We expect you also to keep the time of the other men, to make out the payrolls and attend to the correspondence in shipments of carbides and the receipts of lime and coke. . . . We will pay you $25 per week. . . ." Mr. Kenan states that he accepted the job with alacrity. Thus he entered the electrochemical industry.—ED.]

Schenectady, New York
September 24, 1951

I prefer looking ahead to reviewing the past. I am still interested in the whole of Creation. Electrochemistry seems to be a fine approach to it. Appreciating the creation-as-is should be the supreme effort of man. Apparently the human brain itself is something electrochemical created in man. I like to say "constructed by himself." Our inquisitive work stretches and arranges the wires that make up the brain. All our sensations are electrochemical messages along nerves. They are stored somehow in our subconscious and consciousness; and it is marvellous that a fellow can think about his own mind, as he can contemplate a photograph.

The 200-in. telescope shows the whole universe to be forever expanding. That agrees with our local observations too. It has always been so. Notice, also, how fittingly true it is that the smallest things in the universe are expanding too. Shortly after the ECS was established, all atoms expanded and the electron was disclosed. Now "Electronics business" is over two billion a year. Also, the electrons now serve to increase the expansion by microscopes, from about 2,000 to 100,000-fold. Here are *electrical* parts in the process with fine *chemical* development in the invisible shadows.

It seems humanly impossible to fully appreciate the creation as we find it. But that is reason enough to forever try to do so. What Emerson called the Chaos, which man should tame, may all be only in our feeble minds.

What is really natural is the recognizable, universal, orderliness, the dependency, and the fine, fixed qualities of all parts of the creation itself.

I am led to accept the English Poet Laureate Robert Bridges' view expressed in "The Testament of Beauty" that "Conduct lies in the masterful administration of the unforeseen." And I'd like to add—Creation is never as chaotic in the future, as it has always been in the past.

Lovingly yours,
WILLIS R. WHITNEY

The first seal of the Society appeared on the title page of Volume 48 of the TRANSACTIONS in 1925. The design was decided upon by an Emblem Committee after receiving more than one hundred suggestions submitted by the membership at large. The seal embodies the Weston standard cell, symbolic of electrolysis, and an electric arc, representing electrothermics. It was revised in 1930 when the Society was incorporated under the name The Electrochemical Society, and now appears as shown above.

The First Decade

AN ACCOUNT OF THE FOUNDING AND EARLY DAYS OF THE SOCIETY

"The development of the electrochemical industries and the large increase in the number of electrochemical specialists has made formation of the Society imperative." Thus wrote Professor Joseph W. Richards, first President of the Society, on page 1 of Volume 1 of the TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY. On October 19, 1901, a letter was addressed to thirty residents of the United States believed to be especially interested in electrochemistry, inviting their attendance at a preliminary meeting to be held at the Engineers' Club, 1122 Girard Street, Philadelphia, on November 1, 1901, to consider the organization of a National Electrochemical Society. The meeting was attended by ten men, many of those unable to come having sent letters expressing their interest. The consensus of the group favored the formation of a Society if seventy-five prospective members could be secured. Committees were appointed for membership, meeting and papers, constitution and by-laws, and finance.

JOSEPH W. RICHARDS
First Society President

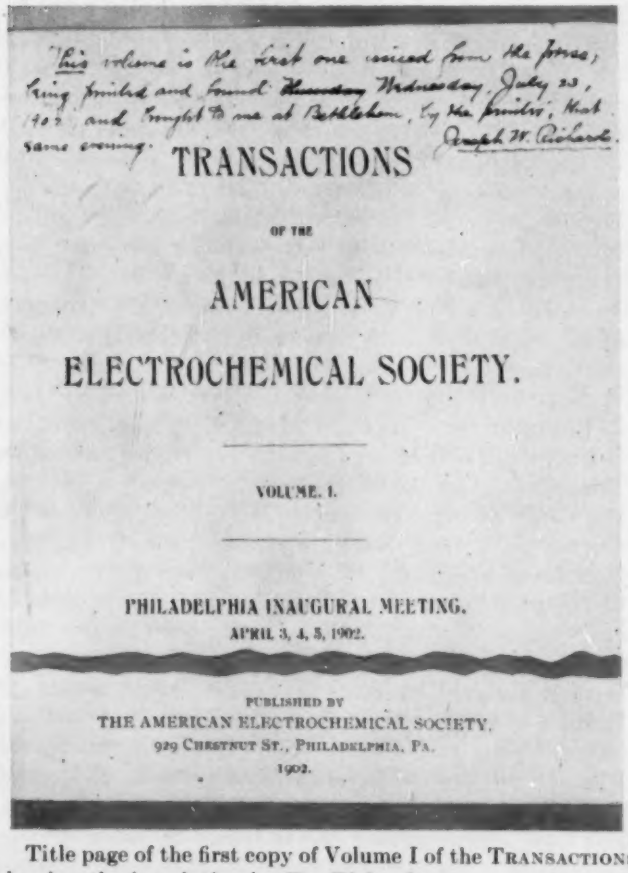
On November 25, 1901, the following letter was addressed to all members of the American Chemical Society, the American Institute of Electrical Engineers, and such other persons as were known to the Committee to be interested in the development of electrochemistry.

"Dear Sir:

The products of electrochemical industries in this country at the present time amount to about $100,000,000 per year. The growing importance of these industries and the fact that scientists and engineers interested in electrochemistry are now distributed among at least half a dozen different societies and, therefore, have no common medium of communication, suggested the formation of an American Electrochemical Society on the same general plan as the American Chemical Society and the American Institute of Electrical Engineers.

"A preliminary meeting in the interest of such an organization was held November 1, 1901 at the Engineers' Club of Philadelphia, Professor J. W. Richards, Vice-President of the American Chemical Society, acting as Chairman, and Mr. Carl Hering, Past President of the American Institute of Electrical Engineers, as Secretary. All of those present were heartily in favor of forming such a society and numerous encouraging letters were received from all parts of the country, those from representatives of the electrochemical industries being especially favorable. It was unanimously decided that such a society should be founded as soon as a sufficient number of members could be obtained to insure success. Committees were appointed to secure members and to arrange for a meeting in the near future at which the Society should be formally organized. It was the opinion of those present at the preliminary meeting that the annual dues should not exceed $5 and that there should be only one class of members.

"The bringing together in this way of those engaged in the scientific study of electrochemistry, and the practical engineers and pioneers of the industry, will be of inestimable value to both.


This volume is the first one issued from the press, being printed and bound Thursday Wednesday, July 23, 1902 and brought to me at Bethlehem, by the printer, that same evening. Joseph W. Richards.

TRANSACTIONS

OF THE

AMERICAN

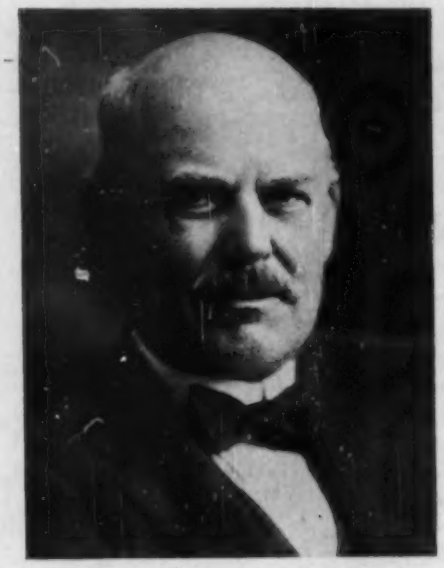
ELECTROCHEMICAL SOCIETY.

VOLUME I.

PHILADELPHIA INAUGURAL MEETING.
APRIL 3, 4, 5, 1902.

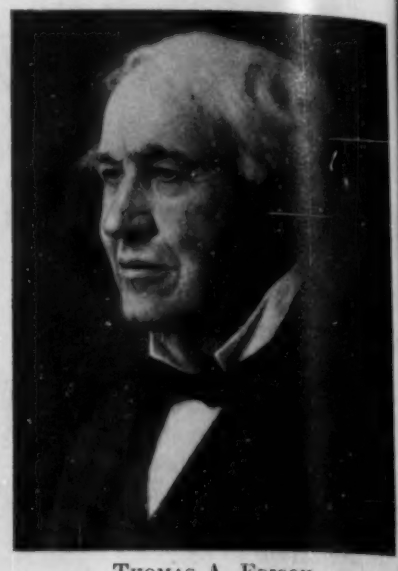
PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY,
929 CHESTNUT ST., PHILADELPHIA, PA.
1902.

Title page of the first copy of Volume I of the TRANSACTIONS showing the inscription by Dr. Richards.



EDWARD GOODRICH ACHESON
Charter Member, and Founder of the Acheson Medal; President 1908–09.

EDWARD WESTON
Honorary Member, and Founder of the Weston Fellowship.



THOMAS A. EDISON
Honorary Member, joined The Electrochemical Society in its second year.

"The undersigned Committee of Membership earnestly solicits your cooperation and asks you to notify the chairman, Dr. Charles A. Doremus, 17 Lexington Avenue, New York, before December 31st, that you can be depended upon to become a charter member.

Yours very truly,
Charles A. Doremus, *Chairman*
W. D. Bancroft,
J. W. Richards,
E. F. Roeber,
C. J. Reed."

The organization meeting was held on April 3, 1902 at the Manufacturers' Club, Philadelphia, with fifty-two in attendance and applications from 337 to become charter members. These were residents of thirty-six states and eight foreign countries, a most gratifying response to the efforts of the Membership Committee. A list of these members in Volume I of the TRANSACTIONS provides a fascinating Who's Who of men prominent in university and industrial circles at the beginning of the century. In addition to the nine known surviving charter members, messages from all of whom appear in this issue, there is to be noted in the catalog of charter members such distinguished names as: E. G. Acheson, F. M. Beckett, C. F. Burgess, H. S. Carhart, Herbert H. Dow, G. B. Frankforter, Charles M. Hall, Carl Hambuechen, Carl Hering, William Hoskins, Dugald C. Jackson, Professor Dr. George Kahlbaum, Louis Kahlenberg, Professor J. W. Langley, Victor Lenher, Morris Loeb, H. A. Metz, W. Lash Miller, Samuel P. and Samuel S. Sadtler, Elmer A. Sperry, N. Tesla, F. J. Tone, L. A. Voorhees, Frank N. Waterman, Charles A. Stone and E. S. Webster of Stone & Webster, and Edward Weston. To these, within the first five years, were to be added as members such well-known people in industry as Leo Baekeland, Thomas A. Edison, Charles P. Steinmetz, Abraham Van Winkle, William H. Nichols, S. Cowper-Coles, J. G. White, Elihu Thomson, Maximilian Toch, David Wesson, Heinrich Heraeus, P. L. T. Heroult, E. K. Berry, and H. B. Coho. From the academic world were such recruits as E. F. Kern, Henry M. Howe, Charles Baskerville, L. M. Dennis, J. E. Mills, J. L. R. Morgan, Samuel W. Parr, George A. Hulett, Theodore W. Richards, Herman Schlundt, E. P. Schoch, Edgar F. Smith, F. C. Mathers, and A. F. Ganz.

Minutes of the organization meeting record unanimously favorable action on the motion that "we now proceed to organize the American Electrochemical Society." The Constitution and By-Laws proposed by the Committee were adopted. The acting chairman, Professor J. W. Richards, was unanimously elected President and C. J. Reed, according to Carl Hering, the prime mover in the organization of this Society, was elected Secretary. Hall, Kahlenberg, Carhart, Bancroft, Doremus, and Whitney were made vice-presidents, and Hering, Weaver, Roeber, Acheson, Weston, Sheldon, Reber, Sadtler, and Mailloux were elected managers, with Pedro G. Salom, treasurer. "On motion the thanks of the Society were voted to the gentlemen who gave their time and energy to establishing this Electrochemical Society."

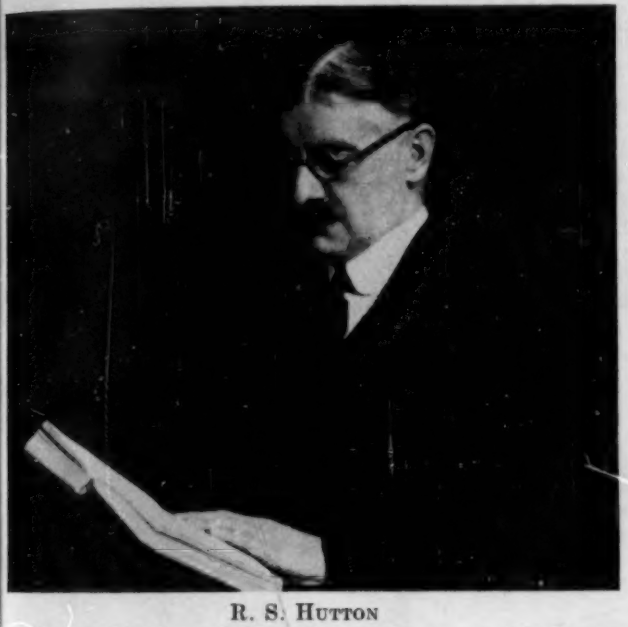
On the following two days, twenty technical papers were presented before the new Society on such diverse subjects as: A New Zinc Bromide Storage Battery, the Continuous Electrolysis of Solutions of Metals, the Electrolytic Rectifier, the Nascent State, the Electrolytic Refining of Composite Metals, the Novel Concentration Cell, Current Electrochemical Theories, and a University Course in Electrochemistry. It is of interest to note that a Committee on Advertising consisting of Richards, Doremus, and A. von Isakovics as Chairman set out to procure advertising for the TRANSACTIONS, and for the two volumes published in 1902 sold sixteen pages for a total of $380. Advertising was carried on the back pages until 1916.

The second meeting of the Society was held at the International Hotel at Niagara Falls, New York, in September 1902, with 117 members and 47 guests. The President presented the following letter from the well-known J. H. Van't Hoff and Dr. Böttinger, President and Vice-President respectively, of the Deutsche Electrochemische Gesellschaft: "Your kind letter of greeting of 28 April reached us in Würzburg just after the close of our general meeting but in time to lay the same before our members during the festival dinner.

"From all present, the formation of the American Electrochemical Society was greeted with particular pleasure and we were instructed to convey the heartiest congratulations of

our Society to you, to express our most earnest hopes for its prosperity and development and at the same time to assure you that we will always follow your work with the greatest interest and that we sincerely trust that a continuous close and amicable connection will remain between ourselves and your highly esteemed Society. May the result of our united work tend to promulgate the further advance of our particular science and the technical utilization of our researches for the benefit of the world at large. We trust that you and your friends will maintain and preserve your kind sentiments for us under our new name, especially as we assure you that our interest in electrochemistry will be maintained in the future as earnestly as in the past. . . ."

President Richards then introduced Dr. Fritz Haber of the Technical School of Karlsruhe, Germany, who was present as the guest of the Society and the official representative of



R. S. HUTTON

Charter Member, Goldsmiths' Professor of Metallurgy, Cambridge University, and 1933 Richards Memorial Lecturer.

the Deutsche Bunsen Gesellschaft. Dr. Haber presented the greetings of that Society and read a letter from its President.

It was reported that thirty-five new members had been added to the Society and that there were twenty-four applications pending. Following the presentation of twenty-one technical papers before the Society, the following resolution was adopted: "WHEREAS: The American Electrochemical Society in convention assembled recognizes the great international importance of the Louisiana Exposition and feels it will do much in placing before the peoples of the world a true picture of our national progress, and WHEREAS: In no branch of our scientific or industrial progress have greater developments taken place recently than in the field of electrochemistry, *Resolved* that the American Electrochemical Society hears with great satisfaction the announcement that steps are being taken looking to the organization of a fine and comprehensive exhibit in the group of electrochemistry and offers assurances of hearty good will and cooperation in the accomplishment of this much to be desired end."

Dr. E. A. Byrnes stated that a company developing one of the largest water powers in the country authorized the statement that it would furnish free electrical energy in indefinite amount for a considerable period for any industry locating with that company.

The third meeting of the Society was held in April 1903 at the Chemists' Club in New York with an attendance of 260. Twenty-eight papers were presented and many distinguished members were in attendance, among whom were Thomas A. Edison, H. W. Wiley, Leo Baekeland, etc. A feature of the meeting was the reception and banquet at the German Liederkranz. There were present among other invited guests Dr. Walter Nernst, of Göttingen, Germany, Dr. Charles F. Chandler, of Columbia University, and Dr. H. W. Wiley, all of whom responded to toasts.

On one evening the Society was the guest of the American Institute of Electrical Engineers and listened to a lecture by William J. Hammer on "Radium and Other Radioactive Substances with a Consideration of Phosphorescent and Fluorescent Substances. The Properties and Applications of Selenium and the Treatment of Disease by the Ultraviolet Light." This address, seventy-two pages in length, appears in Volume III of the TRANSACTIONS and its presentation may have given rise to the present custom of the Electronics Division of scheduling time out for a "stretch" during a technical session.

The technical sessions of these early years were fully participated in by members of the audience, and the subjects covered a wide range of theoretical and practical interest. When Wilder D. Bancroft discussed "The Present Status of the Electrolytic Dissociation Theory," there was a long and heated discussion by F. A. Lidbury, C. J. Reed, Professors Carhart, Richards, and W. Lash Miller.

During this period and the years that followed, papers bearing on important developments of a practical nature, as well as of a scientific character, were presented before the Society. For example, the classical work of Carhart and Hulett on standard cells was presented; F. J. Tone described the first production of silicon; W. R. Whitney presented papers on colloids, arcs, and other diverse topics illustrative of his imaginative mind. Bancroft was a frequent contributor of papers on such diverse subjects as electrolytic refining of copper and the purification of cobalt and nickel, the chemistry of electrochemistry, the electromotive force of alloys, the aluminum rectifier, chemistry of electroplating, and the rotating diaphragm.

President Richards reported at the fourth general meeting of the Society that the number of members had nearly reached the 600 mark and that the Board of Directors was proceeding to draw up regulations for the establishment of local sections as the result of a request to establish such a section at the University of Wisconsin.

In September 1904, the Society met at St. Louis in response to an invitation issued a year earlier by the chief of the Electrical Department of the World's Fair. President Carhart in opening the meeting spoke as follows: "This is to be a joint meeting with the Bunsen Gesellschaft of Germany and the Faraday Society of England. We congratulate ourselves upon having present as a delegate from the Bunsen Gesellschaft Dr. Hans Goldschmidt. Dr. J. W. Richards has been appointed delegate from the Faraday Society of England." Dr. Goldschmidt in responding extended the best wishes of his Society to the two sister Societies for the success of the joint meeting. He pointed out that the German and English Societies were named for two of the most distinguished scientists of the last century, men who knew how to extricate from nature its most intimate secrets.

After greetings from Dr. Richards who spoke on behalf of Mr. Cowper-Coles for the Faraday Society, President Carhart said: "The American Electrochemical Society is always

interested in the youngest member of the family of electrochemical societies and I think the Faraday Society is younger than this Society by a few months. We are interested in the success of this Society in England and many of us take great pleasure in going to England from time to time and hope to have an opportunity of attending the meetings of the Faraday Society in the future."

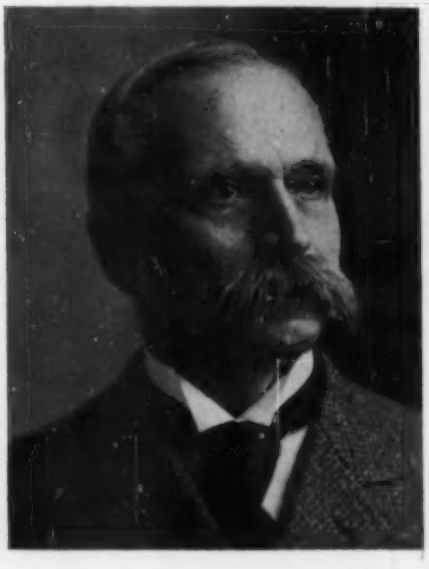
In the technical program at St. Louis were, among others, papers by Ostwald, J. W. Richards, Fritz Haber, P. L. T. Heroult, and one by Dr. Goldschmidt entitled "Aluminothermics" in which he described the thermite process and its applications. He stated that the process had been used to advantage by the Russians for the repair of ships damaged by the Japanese in the recent war. Finally, he pointed out that one of the principal applications of the process should be the welding of rails.

The electrochemical exhibits were one of the chief attractions at the St. Louis Fair. These consisted of apparatus contributed by prominent German electrochemists: Kohlrausch, Ostwald, Nernst, Abegg, Heraeus, and others. There were batteries, dry cells, storage batteries, electrolytic alkali, chlorine, bleaching powder, calcium carbide, carborundum, silicon, graphite, and metallic aluminum and its compounds.

In the spring of 1905, the Society met in Boston and Cambridge and were the guests at lunch on one day of President Elliott of Harvard University and on the second day of President Pritchett of Massachusetts Institute of Technology. Apparently there were a number of plant trips and a visit to Wellesley College, the regents of which were thanked "for their kindness in showing their plants and other interesting things to the Society and its guests." President Elliott spoke of the great importance of a borderland science such as electrochemistry. There were twenty-nine papers presented and President Carhart in closing the meeting said: "... a remark was made by some of the electrical journals at the time of the organization of this Society three years ago, when we were congratulated upon the quality of papers presented at the first meeting, that it remained to be seen whether the Society would be able to keep up such a program for successive meetings. Now, I feel personally the Society may certainly congratulate itself that the product, so to speak, has not been exhausted."

At its eighth meeting at Lehigh University, President Bancroft stated that "... What with the University on the one hand and the great technical works on the other, you have a happy combination of education and application which we hope is one of the strong features of our own Electrochemical Society. It is also a pleasure to recall that we are indebted to Lehigh University for one of the prime movers in the founding of the Electrochemical Society who was at the same time our first President, J. W. Richards. I remember that at the time the Society was founded there was a good deal of discussion whether we were really a chemical society or an engineering society; under those circumstances it seems doubly fortunate that we should meet here at Lehigh University where the late President was a chemist and the present one was an engineer."

At a meeting of the Board of Directors in February 1904, it was decided to grant the Secretary a salary of $500 per annum and to allow $250 per annum for all clerical work. It was further decided to pay the Secretary's transportation to and from national meetings and to give him $5 for each day of the meeting and for one day preceding it. In spite of this generosity, Secretary C. J. Reed declined re-election.



CHARLES F. CHANDLER—Professor of Chemistry at Columbia University; Dean of American Chemists, and Honorary Member of this Society, *left*.

WILLIS R. WHITNEY—Charter Member, and President in 1911–12; for many years Vice-President and Director of Research at General Electric Company, *right*.

The ninth meeting of the Society was held at Cornell University in May 1906, where Professor Bancroft, as a member of the faculty, welcomed the Society and responded for the Society as its President. Gustave Gin of Paris, France, was awarded the Frenzel Prize of $250 for the best essay on "Practical Methods of Treating Rare Minerals Found in America and Extracting Rare Metals Therefrom." This was published in three parts in subsequent volumes of the TRANSACTIONS.

At the tenth meeting held at Columbia University in October 1906, the eminent Professor Charles F. Chandler, an honorary member of the Society, addressed the gathering as follows in part: "Mr. President, and fellow members of the youngest scientific organization which I think we have in this country, and the organization which I think is going to prove, if possible, the most important; it gives me great pleasure to welcome you to Columbia University.

"I have not prepared any speech ... but there are many ideas that naturally associate themselves with electrochemistry. It has already worked such a revolution in many branches of chemical industry that it seems destined to change entirely the character of a large proportion of chemical operations.... In old times in the handling of metals, heat was the agent: terrible heat, scorching furnaces, workmen obliged to strip to the skin, handling enormous heavy rakes and hoes.

and pushing them into those terribly hot furnaces to rake the molten metal, expending their physical energy to an exhausting degree and heating their poor bodies until they became feverish. Now, you go into an establishment like the Pittsburgh Reduction Company's works [later to become the Aluminum Company of America—ED.] and there is hardly anything to do. Still more striking, if you enter the works of the Castner Company, where sodium is being manufactured, or the Saltville Company's works at Niagara Falls, where caustic soda is manufactured, the change is illustrated. . . .

"The aluminum factory illustrates the wonderful effect of electrochemistry in accomplishing economical results. You are all familiar with that industry and know how many different processes were attempted and how strenuous many of them were and how dangerous some of them were on account of the possibility of explosion. And then Charles M. Hall, of Oberlin College, came into the field and put his young mind on the problem of making aluminum . . . and came to the conclusion that the only way was to make use of a solvent for alumina, free from water. . . . He found that melted cryolite would take up alumina to the extent of 25 per cent of its weight. . . . And the next step was whether he could electrolyze the aluminum out of this solution. And he found it could be done without any difficulty whatever, and on reducing the discovery to practice he found it not necessary to apply any external heat. . . . And so this problem which had engaged the attention of scientific chemists for over fifty years was solved by this youth so successfully as to make aluminum a rival of copper in the industries. . . .

"I do not know how much Mr. Hall is in the way of telling of the operations of those furnaces, but there are one or two things which I think I may tell without violating any confidence. Of course, that melted cryolite is very hot and it is very scorching to the workmen and, in looking after some way to protect the men from the heat, the remarkable discovery was made by Hall that when pulverized coke was put on the melted cryolite it does not wet it. The pulverized coke sheds melted cryolite just as a duck's back sheds water, and no matter how much you stir the coke up with the melted cryolite it always comes up to the top and is dry and black, and that preserves the heat and serves as a comparative non-conducting barrier between the heat and the faces of the workmen. . . . This is the thought that came into my mind as I was invited to say something to you; the wonderful effect of electrochemistry in simplifying these metallurgical operations, of accomplishing the same results in a great deal better way and saving the expense of the wear and tear on human beings who are obliged to watch the apparatus and machinery.

"I think, therefore, it is a very valuable addition to our professions to have electrochemistry as a special combination of chemical with physical science and engineering. Of course, every time a new association of this kind is formed the members of the old association are a little sorry. When we proposed to have a [American] Chemical Society [in 1876], the old Lyceum of New York was very unhappy about it. A few devoted men had been struggling along for years in New York City to encourage an interest in science, and a few devoted scientists had been in the habit of meeting in a little room downtown and calling themselves the Lyceum of Natural History. Of course, as the name indicates, they devoted their time chiefly to discussing bugs and every kind of animal and plant, and the chemists did not find it particularly interesting. The chemist would deny himself some social entertainment and go down and meet a dozen enthusiastic zoologists, and they would talk about the difference in the shapes of clam shells from different parts of Long Island; and so the chemists concluded that it would be a good thing to have a chemical society, and they were lachrymose in the other society. They felt we were deserting the flag, and when the Electrochemical Society was started there were some

A distinguished group of members abstracted from picture taken at Montreal Meeting in September 1922. *Left to right*, back row, are Former Presidents HOWARD PARMELEE and CARL HERING, R. J. MCKAY, Former President R. M. BURNS, and HENRY HOWARD. Front row: Former Presidents C. G. SCHLUEDERBERG, COLIN G. FINK, W. LASH MILLER, WILDER D. BANCROFT, F. A. LIDBURY, and WILLIAM BLUM.

tears shed in the Chemical Society for fear that it would diminish interest in our Society, but I do not think it will have that effect.

"You know the English people who celebrated [recently] the jubilee of Sir William Perkin were very unhappy when they heard we were going to have a jubilee over here. They said, "Come over to England." They became reconciled, however. When we were going to have a jubilee here, the Boston chemists thought they would not come here but have a jubilee in Boston. We were a little disappointed at first, but we said afterwards it is all for the good of the cause, which is to honor Sir William Perkin and to magnify the importance of chemistry. Whenever we can get together in any locality whatever, it helps the cause, and the more societies of this kind that we can have the better it is for the cause of science. The value of science will be more thoroughly recognized, and support will be given to scientific and educational enterprises; so, as one of the very earliest members of the American Chemical Society [He was actually chairman of its organization meeting.—Ed.], I congratulate you gentlemen

Colin G. Fink—Secretary Emeritus of the Society; President in 1917–18; Society Secretary and Editor, 1921–47.

on having united to form an Electrochemical Society, and I am proud to have become a member of it, and I welcome you to Columbia, and the oftener you come and the longer you stay the better we shall like it."

Papers read at the meeting had to do mainly with pyrometry, aluminum, and magnesium cells.

Finally, the members attended a smoker given to Sir William Henry Perkin by the chemists of New York City. The first impression of the Perkin Medal had been presented to Sir William on a previous evening.

The eleventh meeting of the Society at the University of Pennsylvania, in May 1907, was addressed by Professor Edgar F. Smith as the University's Vice-Provost, who said in greeting the group: "... It is a matter of great interest to us that this Society at its formation saw fit to hold its first meeting at the University of Pennsylvania. Those who are familiar with the history of chemical teaching in America know that the first chemical society in America was founded in Philadelphia, and by those who were engaged in the teaching of chemistry in our University. This was in 1792. In 1812, the second chemical society in this country was founded here in Philadelphia and was conducted by professors and students of our University. At the founding of the American Chemical Society in 1874, at the grave of the great Joseph Priestley, it was the professor of chemistry in this University who made the suggestion that a national chemical society be formed; so that the University has always had profound interest in things chemical. [The organization meeting of the Society occurred two years later in New York.—Ed.] Hence, it is a matter of no little moment that this, the youngest of the chemical societies, ... has held its first meeting at the University and now its eleventh meeting.... The great Robert Hare, who assumed the duties of the chair [of chemistry] in the year 1818, did much that would be of interest to us Had there been an American Electrochemical Society in that day, he no doubt would have been a most active member.... He devised the deflagrator, with which instrument Benjamin Silliman, the elder, was able to melt and volatilize carbon, as he said. The deflagrator was the forerunner of the Bunsen battery. As we read the researches of Michael Faraday and observe how he sought for something superior to the old Voltaic pile, he finally admits that the deflagrator of Robert Hare was the thing needed for his work. He used it and acknowledges his great indebtedness to him for that discovery. Again in 1838, Robert Hare, after carefully scrutinizing the work of Humphrey Davy on the isolation of the alkaline-earthy metals, set his deflagrator to work upon a solution of calcium chloride, using mercury as the cathode, obtaining an amalgam, which he afterwards distilled and got the metal calcium, of a silver-gray color, of a specific gravity nearly equal to that of the calcium which has been recently isolated, and was able to give its properties more correctly than had ever been given before."

Officers of the Society for 1909

President
L. H. Baekeland, Ph. D.

Past-Presidents
Prof. C. F. Burgess — Dr. E. G. Acheson

Vice-Presidents
C. P. Townsend — F. J. Tone
Dr. Chas. A. Doremus — Carl Hering
Dr. W. R. Whitney — Dr. W. D. Bancroft

Managers
Dr. E. F. Roeber — A. von Isakovics
Dr. L. Kahlenberg — Prof. S. A. Tucker
S. S. Sadtler — E. R. Taylor
F. A. J. Fitzgerald — Dr. W. L. Miller
Dr. W. H. Walker

Treasurer
Pedro G. Salom

Secretary
Prof. Jos. W. Richards

Officers of N. Y. Section for 1909

Dr. E. F. Roeber, *Chairman*
Alois von Isakovics, *Secretary-Treasurer*

Executive Committee
Dr. L. H. Baekeland — Edward A. Colby
E. A. Sperry, E. E.

Page from the dinner Souvenir of the New York City Meeting, October 29, 1909, at Hotel Cumberland, showing the officers of the Society for that year. This booklet was bound in an attractive aluminum cover. Dr. Doremus acted as Toastmaster for the elaborate seven-course dinner.

A group of Past Presidents on the occasion of the award of the Acheson Medal to Charter Member F. J. TONE. *Left to right*: COLIN G. FINK, F. J. TONE, FRANCIS C. FRARY, AND F. M. BECKETT.

An important feature of the twelfth general meeting, held in New York City in October 1907, was the paper by Edward Goodrich Acheson on deflocculated graphite.

The papers of the thirteenth meeting, held in Albany in the spring of 1908, and of the fourteenth meeting, held in New York City the following October, had to do mainly with the subject of corrosion of metals and firmly established the Society's interest in this subject.

The first meeting of the Society outside of the United States was held at Niagara Falls, Canada, and was the first of many meetings in that hospitable country. At this meeting, President Acheson introduced Dr. Eugene Haanel, Director of the Department of Mines, who spoke as follows: "It gives me pleasure to welcome you on behalf of Canada for your first meeting on Canadian soil. In connection with the subject which I am about to present to you, the Examination of a New Furnace Invented in Sweden for the Production of Pig Iron by the Use of Electrical Energy, I desire to make the statement that we are only on the outskirts of the development and discoveries of that extremely important branch of electrometallurgy which concerns itself with the extraction of metals from their ores by the heat resulting from the transformation of energy. . . . When I look into the future, it does not seem unlikely to me that a time may come after the richer and more easily treated iron ores have been exhausted and only refractory ores remain when those magnificent stacks at Pittsburgh and in England will stand as monuments of a departed process of smelting iron ores. . . ."

President Acheson in his presidential address pointed out the importance of electrochemistry in the conservation of our natural resources. Among the forty-five papers presented at the meeting, many were included in a symposium on the electrometallurgy of iron and steel.

Many of the papers before the eighteenth general meeting of the Society held in Chicago in 1910 were on the subject of storage batteries.

For the twentieth general meeting, the Society went again to Canada, this time to Toronto with President Willis R. Whitney in the chair.

For its twenty-first general meeting, the Society returned to Boston in April 1912. President W. R. Whitney chose the subject Electrical Conduction which served as an introduction to a valuable symposium on this subject. Contributions were made by such well-known professors as O. W. Richardson, D. F. Comstock, and Stewart J. Lloyd.

Professor W. LASH MILLER on his way to a meeting of Section Q is stopped by Professor BANCROFT making a point.

When the Society met in New York City for its twenty-second meeting, it was again addressed by the venerable Professor Charles F. Chandler of Columbia University who greeted the assembly in the following characteristic manner: "When I see so many chemists gathered together it carries my memory back to the days when there were not so many chemists in the whole United States as there are now in this room, to a time in fact when there was no place in the United States where a man could get a chemical education. That is within my recollection. I entered at Harvard University in

1853 fascinated with the idea of being a chemist. I stayed there a year receiving practically no instruction in chemistry. There were a half dozen others there like myself taken with the idea of becoming chemists, but the only practical instruction we obtained was what we got from each other. I have often wondered, thinking over that year in the Lawrence Scientific School, whether we have really improved matters by the methods we have now adopted for teaching chemistry. In those days, the student had to do the work and if he had not enough interest in the subject, enough character to do the work, he dropped out and went into something else. Now we open our doors and we take students in by the hundreds who say that they want to be chemists and we do all the work. . . ."

Among the many interesting and varied papers were contributions from such well-known authors as W. D. Bancroft, C. F. Burgess, W. K. Lewis, J. H. Hildebrand, T. W. Richards, G. A. Hulett, E. W. Washburn, and Colin G. Fink.

The foregoing running account from the official records gives the flavor of those early days of the Society. It portrays the activities and expectations of those energetic, imaginative men who as leaders in the academic and industrial world of their day founded and led the Electrochemical Society. Closely related by technical interests, they developed a discussion habit which has continued to characterize the general meetings of the Society. Finally, there was social intimacy and fellowship which led to that informal body known as Section Q. According to former President A. T. Hinckley, Section Q was organized by Professor W. Lash Miller sometime prior to 1910. Hinckley states "Professor Miller provided all members with lighted candles at an appropriate time in the evening that they might file in lighted procession to visit the hydraulic laboratories. This resulted in considerable gaiety and the ceremony was perpetuated for a number of years. In addition to Lash Miller, F. A. Lidbury, F. J. Tone, F. A. J. Fitzgerald, L. E. Saunders, and F. M. Beckett were all enthusiastic participants as were many of the General Electric men from Schenectady, including Dr. Willis R. Whitney and his associates from the research laboratories there. Ned Crosby from Detroit and George Heise from Cleveland were others who joined the group enthusiastically as the years went on. Many of the electrochemical songs which were used, particularly in the electrochemical show at the Detroit meeting in honor of Dr. Richards, were composed jointly by F. A. Lidbury and Ned Crosby. This same group was responsible for much of the gaiety which attended the initial train trip to Muscle Shoals."

According to the proceedings of the fifteenth general meeting, "a smoker was inaugurated at nine o'clock (May 7, 1909) terminating with an interesting session of Section Q which was enjoyed by everyone, even those 'hit' the hardest." The frontispiece of Volume 20 of the TRANSACTIONS presents a candlelight parade of Section Q accompanied by the bagpipe and would seem to confirm Hinckley's recollections of the nature of this organization.

Oldtimers will remember the gracious hospitality of the leaders of Section Q, and particularly of F. A. Lidbury and others of the Niagara Falls Section. Even weary travelers of more recent times have been the fortunate recipients of this traditional hospitality.

This history of persons and events of the early days leads to an understanding of how it has come about that The Electrochemical Society grew and has continued to make notable scientific and industrial contributions during its first half century. No one doubts that it will be the instrument for the accomplishment of even greater things in connection with the expanding chemical industry of the next fifty years.

—RMB

FIFTIETH ANNIVERSARY MEETING

The Electrochemical Society

Philadelphia, May 4, 5, 6, 7, and 8, 1952

Sessions on

Electric Insulation, Electrothermics, Instrumentation, Luminescence, Methods of Applying Phosphors, Rare Metals, Theoretical Electrochemistry

Headquarters at the Benjamin Franklin Hotel

Papers are now being accepted for the meeting to be held in Philadelphia. Abstracts (not exceeding 75 words in length) are due at the Secretary's Office, 235 West 102nd Street, New York 25, N. Y., *not later than February 1, 1952.* Complete manuscripts shoud be sent in trplicate to the Editor of the JOURNAL at the same address.

Current Affairs

Fine Programs Mark Fall Section Meetings

Philadelphia Section

The first meeting of the 1951–52 season of the Philadelphia Section was held on Wednesday evening, November 7th, at the John Harrison Laboratory of Chemistry of the University of Pennsylvania. The meeting was preceded by an enjoyable informal dinner where members and guests had the privilege of meeting the speaker of the evening. The meeting was conducted by Dr. John F. Gall, the new chairman of the Section.

Dr. Gall welcomed the 50 or 60 members and guests in attendance and, for the benefit of the guests, spoke briefly describing The Electrochemical Society. He recommended the Society to qualified persons who were not members and encouraged them to consider joining.

Dr. Gall then introduced Dr. Hiram S. Lukens who is the general chairman of the National spring convention, the 101st meeting, scheduled for May 4 to 8, 1952, and to be held in Philadelphia. Dr. Lukens outlined briefly the present plans of the convention committees. The Philadelphia Section is enthusiastically working on the plans for this meeting, and it is the hope of the Section to make every condition favorable for an outstanding meeting, as is fitting for the Fiftieth Anniversary of the Society.

The speaker of the evening, Mr. F. Curtis Snowden, was then introduced by Dr. Gall. Mr. Snowden is with General Aniline and Film Corporation, where he is engaged in the design and development of new analytical instrumentation.

The subject of Mr. Snowden's address was "The Cathode-Ray Polarograph and Its Application to the Study of Chemical Kinetics." The speaker opened his address by reviewing briefly the history of cathode-ray polarography. The contributions of Mathiason and Nichols, R. W. Müller, and Airey and Randles were presented. The speaker discussed the differences in approach between what he chose to call normal oscillographic polarography and single-sweep oscillographic polarography.

F. Curtis Snowden

The construction and characteristics of the instrument were presented next. The assembly contains a sweep generator capable of applying to the dropping mercury electrode a linear voltage sweep which is continuous from +0.50 to −2.5 volts. Adequate linearity is obtained by using the first three volts of a 300-volt supply. A built-in vacuum tube voltmeter is used for adjusting the minimum and maximum values of sweep voltage. A voltage clipper is included in the circuit to prevent the application of excessive voltage to the electrode. A blanking relay is provided to prevent the focussing of the electron beam on the cathode-ray tube screen except when the input voltages are applied to the deflection plates. The voltage drop across the polarographic cell is maintained independent of the drop across the series current measuring resistor by means of a unique voltage compensating circuit.

Mr. Snowden termed the delay gate the "heart" of the instrument. This unit synchronizes the voltage sweep across the cell with the mercury drop. This is necessary to insure reproducibility of the curve for successive sweeps and to minimize the distortion introduced into the curve by the increase in diffusion current during the sweep interval.

The speaker compared the potential field of application of this method with that for normal polarography. He stated that this instrument is particularly applicable to kinetic studies of reactions that go to completion relatively rapidly. As many as six points may be obtained for a reaction requiring only 30 seconds for completion.

A number of kinetics studies were presented in which the course of the reaction was followed by the new polarograph. These included (1) a rapid light-sensitive reaction, (2) the heat decomposition of a diazo salt, and (3) the formation of an azo dye by a diazo coupling reaction.

The fact that the polarographic trace as obtained by this method gives a peak instead of a plateau was discussed by the speaker. He pointed out that these peaks have some of the properties of a derivative wave and hence might be attributable to some electrical differentiating effect.

A lively question and answer period followed the close of Mr. Snowden's address.

E. L. Eckfeldt, *Secretary*

(*Continued on following page*)

Washington-Baltimore Section

Dr. Mortimer C. Bloom of the Naval Research Laboratory was moderator for the ninth meeting of the Washington-Baltimore Section which was held November 15th, 1951 at the National Bureau of Standards. A series of three talks was given on "The Behavior of Electrons in Solids." The speakers and their topics with a brief abstract are listed below.

Semiconductor Rectifiers

Robert B. Breckenridge

National Bureau of Standards

While there are a number of types of rectifiers known, and a multiplicity of theories to explain the phenomenon of rectification in them, all of the theories suggested by the modern picture of conduction in solids are in agreement on one fundamental point. This primary characteristic is the assumption of the existence of an asymmetric potential barrier somewhere in the system over which the charge carriers will pass more readily in one direction than in the other. Such an asymmetric barrier can be produced in a number of ways. An "artificial" barrier may be produced by placing a very thin insulating film between two metals with different work functions. A "chemical" barrier may be produced at the interface between a semiconductor and a metal by a change in composition of the semiconductor. A "physical" barrier may be formed at a semiconductor metal interface by a depletion of charge carriers from the impurity levels near the semiconductor surface in order to establish a charge equilibrium between the two materials when they are in contact. The most recent development is a *p-n* junction barrier that is established when the type of charge carriers changes from holes to electrons at some point in a semiconductor. All of the theories predict a current flow of the type $I = I_0(e^{e/kT\,V} - 1)$ although they differ in the values suggested for the constant I_0. Much of the difficulty in the application of the theories lies in the fact that an actual physical case may involve a composite barrier where several of the models may be applied.

Luminescent Materials

James H. Schulman

Naval Research Laboratory

A summary of the present state of knowledge of solid luminescent materials emphasized the important effects of temperature and impurity content on the luminescence efficiency of solids, together with the theoretical interpretation of these effects, was discussed in terms of configuration coordinate diagrams and of the energy band picture of crystals. The preparation and characteristics of two important families of phosphors were described briefly. The difficulties that are encountered in interpretation of the general diffuse absorption and emission spectra of solid phosphors were pointed out, most phosphors giving broad emission bands even at liquid helium temperature. Since the group of atoms or ions that emit the fluorescent light is not necessarily the same group that absorbed the incident exciting energy, the problem of energy transfer and transport through a crystal is a very important one. The speaker discussed three mechanisms of energy transfer: by electron and hole migration, by exciton waves, and by sensitized luminescence. A general property of phosphors—the storage of energy and its remission under thermal or optical excitation—was also briefly discussed.

Permeability at High Frequencies

George T. Rado

Naval Research Laboratory

In introducing the subject, the speaker remarked that postwar studies of magnetic permeability at high frequencies were stimulated by the development of radar techniques, the improvement of certain ferromagnetic oxides ("ferrites"), and recent advances in the understanding of exchange forces and ferromagnetic domains. The sustained interest in this subject is largely due to the application of high frequency magnetic phenomena in various circuit elements, and as a tool for the clarification of some basic electronic and atomic interactions occurring in ferromagnetic substances.

The discussion continued with a review of the meaning of permeability at high frequencies. It was shown that the existence of a purely magnetic energy loss, distinct from hysteresis and eddy current losses, requires the description of the permeability by two real numbers, or one complex number. This complex permeability can be measured by determining the two components of the impedance of a toroidal core, cavity resonator, or other circuit element containing the ferromagnetic sample to be tested. A brief summary of domain theory was then given, and the importance of electropolishing techniques for the observation of strain-free domain patterns was noted. It was particularly emphasized that the elementary magnetic dipoles, the electron spins, act like magnetic tops rather than bar magnets.

Finally, the results of two important experiments involving the response of electronic moments to externally applied high frequency magnetic fields were presented and contrasted: (1) Induced ferromagnetic resonance, due to the forced Larmor precession of the whole system of spins in an externally applied, strong, static magnetic field, and (2) natural ferromagnetic resonance, due to the forced Larmor precession of the domains in internal fields and the forced oscillation of the "walls" between the domains. Certain theoretical and experimental problems connected with these two effects were mentioned in closing the discussion.

A very interesting discussion period followed these talks.

J. C. White, *Secretary-Treasurer*

Chicago Section

The Chicago Section was treated to an especially interesting address when they met on November 2nd, at the Chicago Engineers' Club. Dr. R. F. Humphreys, Chairman, Physics Research Department, Armour Research Foundation, spoke on "Nuclear Tracers in Chemical Processes."

In an effort to dispel some of the mystery surrounding nuclear chemistry, Dr. Humphreys presented the fundamental principles involved in the design and execution of tracer experiments. After explaining the properties of the several nuclear particles, he reviewed the many items of equipment which are available for tracer work, emphasizing the fact that many very productive experiments can be performed at a radiation level so low that no unusual protective precautions need be taken. Furthermore, Dr. Humphreys pointed out that equipment for tracer work need not be more expensive than for other widely used techniques.

The enthusiasm displayed during the question period left no doubt that the audience went away from the meeting with a host of new ideas.

Howard T. Francis, *Secretary*

Detroit Section

At its November 16th meeting at Wayne University, the Detroit Section heard an address on the "Merits and

Demerits of Conductivity Theories" by Dr. Lee O. Case, Department of Chemistry, University of Michigan.

In his talk, Dr. Case discussed some of the important conductivity theories and attempted to resolve some of the confusion which exists in this field. It was an informal presentation and provided an excellent opportunity for his listeners to clarify some ideas on conductivity. The question period which followed attested to the lively interest in the discussion.

A. M. LINN, *Secretary-Treasurer*

Midland Section

The second meeting of the season opened with a dinner at the Midland Country Club, on November 15th, honoring our President, Dr. Ralph M. Hunter. The group then adjourned to the Dow Auditorium for the program.

After preliminary motion pictures, Dr. Hunter presented his very interesting talk "What the Pioneers Missed," in which he pointed out the characteristics of the development of electrochemical industry. Since applications of theoretical principles are often misleading, the speaker showed how situations, theoretically difficult to explain, figured in the pioneering of what is today one of the fundamental building-blocks of our entire chemical industry, namely electrochemistry.

The point was amplified by illustrations from the chlorine and magnesium industries. Comparisons with the more publicized and spectacular growth of the electric power industries, and more recently the atomic energy installations, showed the unsung nature of our pioneering and, at the same time, its equally spectacular character and importance.

The data presented led to considerable comment in the question and answer period following the talk.

W. R. PERRY, *Secretary*

New York Metropolitan Section

In one of the largest gatherings in its history, the New York Metropolitan Section enjoyed a social hour and dinner at the Holley Hotel on November 14th. Following this, R. L. Wallace, Jr., of Bell Telephone Laboratories, Murray Hill, New Jersey, spoke on the subject "Some Unusual Properties of the *n-p-n* Transistor."

In a strictly popularized version of an extremely complex topic, the speaker both informed and entertained the audience.

Although theories of transistor action were not discussed, Mr. Wallace attempted to standardize the rather ephemeral unit "Flea Power." It seems that a vigorous flea jumping 50 cm vertically would dissipate no more energy than would a transistor during a minute's operation.

The features of the transistor that make it particularly attractive to circuits engineers are its very small size and weight, its long life, and the fact that it does not require a heated surface as the source of electrons as is the case with a conventional vacuum tube.

During the discussion which followed the talk reference was made to the concept of "holes" or vacancies in the germanium lattice. As an electron moves through the lattice of a semiconductor it leaves a vacancy, which may be considered as bearing a positive charge, behind. Mathematically, it is often more convenient to consider migration of "positive holes" than of negative electrons. The need for extreme purity of the semiconductor was also mentioned. Apparently the spectrograph is too crude an instrument for analytical purposes.

F. A. LOWENHEIM, *Secretary-Treasurer*

India Section

The India Section's third technical meeting for 1951 was held at Mettur Dam on October 27–28, 1951. This was the first meeting of the Section outside Bangalore.

The first day's program commenced with visits to the Mettur Dam and Power House, the Mettur Sandalwood Oil Company, and the Mettur Industries. In the afternoon the members and guests were entertained at Tea. This was followed by a technical meeting with Mr. J. Balachandra in the Chair. Mr. K. Rajagopal (Society member) of the Mettur Chemical & Industrial Corporation, Mettur Dam, read a paper on "Electrolytic Caustic-Chlorine Industry in India."

The speaker gave an account of the development of this industry in India and emphasized the fact that the disposal of the chlorine produced was an important problem to be considered in any scheme for expansion of the industry. The consumption of caustic soda was estimated at 64,000 tons whereas the present installed capacity of electrolytic caustic was only 13,000 tons. Methods for utilizing the chlorine were outlined. He then described the methods of manufacture with special reference to the electrolytic cells in operation at the Mettur Chemicals, namely, the Billiter and Hooker S type.

A discussion followed the talk in which many members participated. The Secretary, Dr. T. L. Rama Char, expressed the thanks of the Section to the authorities of the Mettur Chemical & Industrial Corporation for giving all facilities to hold this meeting, including arrangements for the stay of members at Mettur. The meeting terminated after a vote of thanks to the Chair. The members were then entertained with a film by Mettur Chemicals.

On the second day, the members made a tour through the Mettur Chemical & Industrial Corporation. This visit was of particular interest as the Corporation produces caustic soda and chlorine by the electrolytic method. The program was rounded off with a lunch arranged by Mettur Chemicals.

* * *

The Society has approved the proposal of the Section to issue a *Bulletin of the India Section of The Electrochemical Society*. The Chairman of the Section has appointed an Editorial Committee and Advisory Board for the *Bulletin* and arrangements are being made to bring out the first issue early in 1952.

T. L. RAMA CHAR, *Secretary-Treasurer*

Indian Symposium on Electroplating

The National Metallurgical Laboratory, Council of Scientific & Industrial Research, India, has arranged to hold a Symposium on "Electroplating and Metal Finishing" at Jamshedpur during February 1952. It will cover the theoretical and practical aspects of electroplating, electropolishing and anodizing, and help in disseminating technical information useful to the research worker as well as the industrial plater. A number of electrochemists and electrometallurgists, including members of The Electrochemical Society, are expected to participate in the Symposium.

T.L.R.C.

Correction

In the August 1951 issue of the JOURNAL, page 115C (Notes from India), column 1, line 43, substitute "Vorce" for "Hooker"; in column 2, line 33, for "D. V. Krishna" substitute "D. V. Krishna Rao."

Victor Produces First Phosphorus in Montana

The first elemental phosphorus ever produced in the State of Montana left the Silver Bow electric furnace plant of Victor Chemical Works on November 5th, destined for conversion into phosphate products serving a wide variety of military, industrial, and home needs.

The pioneer tank car of phosphorus was dispatched to the Chicago Heights, Illinois, plant of Victor, which is a major producer of industrial chemicals. The second carload goes to Victor's converting plant in South Gate, California. The company's other electric furnace plants are in Mount Pleasant, Tennessee, and Tarpon Springs, Florida.

The Silver Bow plant is located near Butte. Construction was started about a year ago following a thorough study of phosphorus requirements and analyses of the availability of phosphate rock and electric power used in reduction of the rock into elemental phosphorus. The Silver Bow plant will consume an amount of electric power equal to that used normally in a city the size of Denver.

Victor now has six furnaces in regular production and when the expansion program is completed next year, the company will have increased its phosphorus production and its end-product output approximately 60 per cent over the capacity existing on October 1, 1951. This, it is said, will make the company the world's largest producer of phosphorus and phosphate products.

Electrodepositors' Society Changes Name

Announcement has been made that the Electrodepositors' Technical Society of London is now officially incorporated as a limited corporation and, at the same time, has adopted a new title. It will henceforth be known as the Institute of Metal Finishing Incorporating Electrodepositors' Technical Society Limited.

This step is in accordance with the general policy of the Society to extend its field beyond electrodeposition processes to include metal finishing generally, with which the bulk of its members are vitally concerned. The change, however, will not affect the original aims of the Society which will be pursued with the same interest as formerly.

The Executive Officers and Council of the new Institute remain unchanged.

Philadelphia Historical Exhibit

As a feature of the Fiftieth Anniversary Meeting in Philadelphia, May 4–8, 1952, it is planned to have an exhibit of apparatus and industrial equipment used in the earlier days of electrochemistry. The committee in charge of arranging this exhibit invites the cooperation of members of the Society in providing exhibit material for use during the Philadelphia meeting. Kindly address inquiries to the chairman of the committee: Arthur Osol, Philadelphia College of Pharmacy and Science, 43rd St. & Kingsessing Ave., Philadelphia 4, Pa.

Electronics Division To Offer Abstract Booklet

As a service to members, the Executive Committee of the Electronics Division has made plans to publish an abstract booklet of all papers to be given at the sessions of the Division which will be held at the Philadelphia Meeting (May 4 to 8, 1952). This is expected to include the Symposia on Luminescence, Rare Metals, Phosphor Application, and Instrumentation. The abstracts will average 1000 words and will contain essential tables and figures. It is planned to have the booklet available before the meeting.

To finance this venture, the Committee has decided to assess Divisional dues at $1.00 per year for 1951 and 1952 ($2.00 total). Members paying their dues will be given credit for half of these dues ($1.00) toward purchase of the abstract booklet. The exact cost of the booklet is not yet known; it is hoped that it will not be more than $2.50.

It is essential to know in advance how many members will buy the abstract booklets so that the Division will have some idea of the number to be printed. Therefore, it would be appreciated if all who would find the booklet useful would send prepublication orders to:

J. R. Musgrave
The Eagle-Picher Company
Box 290, Joplin, Missouri

Those who intend to submit papers for the program should write *immediately* to the appropriate Chairman:

Rare Metals: D. M. Wroughton, 707 Gaywood Drive, Pittsburgh 21, Pennsylvania

Luminescence: Roland Ward, University of Connecticut, Storrs, Connecticut

Screen Engineering: A. E. Hardy, R. D. 4, Lancaster, Pennsylvania

Instrumentation: R. H. Cherry, Leeds & Northrup Company, 4901 Stenton Avenue, Philadelphia, Pennsylvania

New List of German Chemical Books Ready

A new catalogue entitled "German Books on Chemical and Cognate Subjects Published 1939–1950" has been announced by Lange, Maxwell & Springer, Ltd., 41–45, Neal Street, London, W. C. 2. This is the Second Revised Edition, and is by A. E. Cummins and S. Vince. It will be sent free of charge, upon request to the publishers mentioned above, to scientific and industrial libraries and to individuals who may be interested.

MEETINGS OF OTHER ORGANIZATIONS

American Institute of Electrical Engineers, winter general meeting, Hotel Statler, New York City, January 21–25, 1952.

American Society for Testing Materials, spring meeting and committee week, Hotel Statler, Cleveland, Ohio, March 3–7.

American Society of Mechanical Engineers, spring meeting, Seattle, Wash., March 24–26.

Greater New York Safety Council, 22nd annual safety convention & exposition, Hotel Statler, New York City, April 1–4.

PERSONALS

WILBERT A. TAEBEL, recently of Eimer & Amend, New York City, has joined the Westinghouse Electric Corporation, at Bloomfield, N. J., as Section Engineer. His work includes the coordination of research and development activities associated with the powder metallurgy of molybdenum.

JOSEPH F. CERNES of Cleveland Graphite Bronze Company's Engineering Division, Cleveland, has been promoted from senior metallurgist to chief metallurgist; at the same time HARRY V. POCHAPSKY was promoted to chief electrochemist from senior electrochemist.

ROBERT D. SCHWARTZ has received the Ph.D. degree in chemistry from the University of Buffalo, and has accepted a position in the Research Department of Electro Refractories and Abrasives Company, Buffalo, N. Y.

HAROLD SILMAN, Chief Chemist of Joseph Lucas Ltd., Birmingham, England, was elected the first President of the newly incorporated Institute of Metal Finishing which now includes the functions of the Electrodepositors' Technical Society (founded in 1925) which it incorporates.

ROBERT W. MANUEL of Cincinnati, Ohio, has accepted a position with Lago Oil and Transport Company, Ltd., Aruba, Netherlands West Indies.

B. K. R. PRASAD, Electric Grid Offices, Government of Bombay, Bombay, India, has been appointed Chairman of the Electrical Section of the Bombay Center of the Institution of Engineers (India).

PETRI BRYK, who was formerly located at Outokumpu Oy, Pori, Finland, is now at Puistokatu 9B, Helsinki, Finland.

SVEN BERGSTROM, president of Nife, Inc., 165 Broadway, New York City, announces that his firm has moved to Copiague, (Box 341), Long Island, N. Y.

LOUIS KOENIG, former Assistant Director of Research at Stanford Research Institute, Stanford, Calif., is now on the staff of Southwest Research Institute, San Antonio, Texas.

JOHN SUMNER of National Carbon Limited, Toronto, Canada, has been transferred to this company's office at 637 Craig Street West, Montreal, Canada.

RALPH J. HOVEY, JR., formerly with Scientific Control Laboratories, Chicago, has joined the staff of the Fansteel Metallurgical Corporation in Chicago.

GEORGE STERN has been elected Vice-President and Technical Director of American Electro Metal Corp., Yonkers, N. Y. Mr. Stern, formerly Research Director for the company, holds many patents, and has had numerous publications in the field of powder metallurgy.

NEW MEMBERS

In November 1951, the following were elected to membership in The Electrochemical Society:

Active Members

MILTON J. ALLEN, National Cancer Institute, Bethesda 14, Md. (Electro-Organic)

CHARLES H. BELVIN, Chromium Corporation of America, 100 E. 42nd St., New York 17, N. Y. (Electrodeposition)

GEORGE L. CLARK, 305c Noyes Laboratory, University of Illinois, Urbana, Ill. (Battery and Electrodeposition)

WILLIAM S. GRAFF, Electric Storage Battery Company, mailing add: Apt. K303, 1415 Clearview St., Philadelphia 41, Pa. (Battery)

WILLIAM M. LANGDON, Graham, Crowley & Associates, Inc., mailing add: 341 E. Ohio St., Chicago 11, Ill. (Battery and Electro-Organic)

DONALD R. MARTIN, Naval Research Laboratory, mailing add: 12 W. Linden St., Alexandria, Va. (Corrosion and Theoretical Electrochemistry)

SVANTE MELLOGREN, National Lead Company, mailing add: 880 Highway 35, Laurence Harbor, N. J. (Electrodeposition)

ROBERT D. MISCH, Argonne National Laboratory, P.O. Box 5207, Chicago 80, Ill. (Corrosion)

FRANCIS ODELL, Surface Alloys Inc. mailing add: 5835 W. 98th St., Los Angeles 45, Calif. (Electrodeposition)

PAUL T. O'REILLY, Amalgamated Battery & Electrical Co., Ltd., P.O. Box 9515, Johannesburg, Transvaal, South Africa (Battery)

NORMAN PARKINSON, Mallory Batteries Ltd., mailing add: 76, Hayes End Dr., Hayes, Middelsex, England (Battery, Electrodeposition, and Industrial Electrolytic)

IDA M. PATTERSON, Naval Research Laboratory, mailing add: Apt. 103, 4614 Livingston Rd., S. E., Washington 20, D. C. (Battery)

GEORGE J. PETRO, Arthur S. LaPine & Co., mailing add: 905 W. George St., Chicago 14, Ill. (Theoretical Electrochemistry)

KENNETH L. SANBORN, General Electric Company, mailing add: 801 Snow Ave., Richland, Wash. (Corrosion)

MORRIS A. STEINBERG, Horizons, Inc., 2891 E. 79th St., Cleveland 4, Ohio (Electrothermic)

CHARLES G. STUPP, The Barrett Division, Allied Chemical & Dye Corporation, 40 Rector St., New York 6, N. Y. (Industrial Electrolytic)

KUSUHIKO TAKAHASHI, Tokyo Electrochemical Industries Co., Ltd., No. 11 Tsuneyoshi-Furushinden, Amagasaki City, Hyogo Pref., Japan (Battery, Electrodeposition, Electronics, Industrial Electrolytic, and Theoretical Electrochemistry)

Reinstatements

WALTER BINAI, Consulting Engineer, mailing add: 3916 N. Parker Ave.,

BOUND VOLUMES

Members of the Society who wish to have their 1951 JOURNALS bound may do so by making arrangements with:

Moore & Company, Inc.
2201 Garrett Avenue
Baltimore 18, Maryland

The collected copies of the JOURNAL should be sent directly to the binder. The binding used will match the 1950 volumes (red simulated leather). The price, including postage, will be $3.25 for binding the complete JOURNALS or $3.75 for binding the technical section and index only. Delivery time will be four weeks after receiving JOURNALS. To avoid error be sure that your return address is clearly marked on the package of JOURNALS sent to the binder.

Requests for this service should be directed to the binder and *not* to the Society.

Indianapolis 5, Ind. (Corrosion, Electrodeposition, and Industrial Electrolytic)

HERBERT SCHMIDT, Dow Chemical Co., mailing add: 1313 Helen St., Midland, Mich. (Corrosion)

Associate Members

WILLIAM C. DAVIS, Sylvania Electric Products Inc., mailing add: 173 Fall St., Seneca Falls, N. Y. (Electronics)

ARTHUR L. GEARY, Chemical Research and Development, Weirton Steel Co., Weirton, W. Va. (Corrosion and Electrodeposition)

GEORGE SKELLY, U. S. Air Force, mailing add: 2109 Green St., Harrisburg, Pa. (Electrodeposition)

D. L. SRIKANTAN, The Cauvery Valley Paper Mills Ltd., mailing add: Palace St., Nanjangud (Mys. St.) India

Student Associate Members

FRANK L. MCGEARY, Aluminum Research Laboratories, Box 772, New Kensington, Pa. (Corrosion)

CLARENCE F. PILLON, JR. Louisiana State University, mailing add: 2519 Jackson Ave., Baton Rouge, La. (Theoretical Electrochemistry)

LAZARUS D. THOMAS, University of Michigan, mailing add: 2210 Maplewood Ave., Toledo 6, Ohio (Theoretical Electrochemistry)

BOOK REVIEWS

LUMINESZENZ VON FLUESSIGKEITEN UND FESTEN KOERPERN by Peter Pringsheim and Marcel Vogel. Published by Verlag Chemie, GMBH, Weinheim, 1951. xiv plus 240 pages, DM 18.60.

The first two parts, comprising 204 pages, are a literal translation of the authors' book which was published in 1943 in English. All of the typographical errors which this reviewer had noted in the English edition have been corrected, but some statements of a minor nature still appear with which the reviewer is not in accord.

Dr. Pringsheim has added a third part of 18 pages on recent developments, with the aim of bringing the book up to date. The topics discussed include measuring devices, some of the new phosphors, efficiency under excitation by high energy particles, fluoresence analysis, fluorescent pigments, fluorescent lamps, and new types of screens for television, radar, infrared signaling, temperature measurements, and scintillation counters. The presentation is suggestive but very brief, and the bibliography could well be longer. The calcium halophosphate phosphors, it should be noted, are well suited for lamps but not for television.

Although the book is not at all as profound or as extensive as other recent books in English, including Dr. Pringsheim's fine and philosophical treatise, "Fluorescence and Phosphorescence," it remains an excellent introduction to the subject, short but clear, concise, and readable. In addition to this merit, this new edition should have a special appeal to German readers because of its presentation of American developments of the past fifteen years or so.

The binding is strong and attractive, and the typography is pleasing, except that the quality of the type leaves, at times, something to be desired. The photographs lack the detail present in the English edition.

GORTON R. FONDA

PRACTICAL ELECTRON MICROSCOPY by V. E. COSSLETT. Published by Academic Press Inc., New York, and Butterworths Scientific Publications Ltd., London, 1951. xiii plus 299 pages, $5.50.

One of the leading British electron microscopists skilfully covers the field of practical electron microscopy. The principles of optical and electron microscopy are well presented in a practical manner which uses a minimum of mathematics. A comprehensive but not too detailed description of commercial magnetic electron microscopes includes many European instruments, not well known in this country. Electrostatic and other types of microscopes are also described. Factors determining micrograph quality are discussed in considerable detail including instrumental and photographic recording limitations. Techniques of specimen preparation peculiar to electron microscopy are thoroughly treated in two chapters dealing respectively with particles, tissues, and sections, and with replica methods used in electron microscopical studies of surfaces. The chapter dealing with present limitations and future prospects is very interesting, even though the prospects do not now lie within the field of practical electron microscopy.

In common with most other texts on the electron microscope, the book does not fairly assess the value of electron stereophotography, which the reviewer feels is often indispensable for the interpretation of micrographs of surfaces, and cannot be supplanted by shadowing methods. Similarly, scattered through the book are many positive statements which are certainly not proved: for example (p. 216), "the extreme simplicity and speed of the single-stage plastic replica greatly outweigh any extra throught that may have to be given to its evaluation,"—a statement with which the reviewer vigorously disagrees. The presentation of opinions as truths or facts is perhaps inevitable in a new pictorial science such as electron microscopy, which is bounding forward into the unknown world of the ultra-small.

To sum up, the book is an excellent introductory text for students of electron microscopy. Many electron microscopists will also want to have it available on their shelves for reference purposes. The simplicity of presentation and lucid writing style will commend the book also to all those interested in the potentialities of electron microscopy as a tool of science.

C. J. CALBICK

RECENT PATENTS

Selected for electrochemists by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

August 7, 1951

Longsworth, L. G., 2,563,729, Method and Apparatus for Control of Boundary Between Electrolytic Fluids

August 14, 1951

Allen, M. J., 2,563,806, Preparation of Substituted Bis-Aminophenyl Ethylene Glycols

Wollentin, R. W., and Nagy, R., 2,563,900, Phosphor and Method of Making

Nagy, R., and Wollentin, R. W., 2,563,901, Phosphor and Method of Making

Zadra, J. B., 2,563,903, Electrolytic Cell for the Deposition of Gold and/or Silver from Solutions

Harrison, T. R., 2,563,931, Rate Responsive Thermocouple

Huntsberger, H. D., 2,563,936, Method of Manufacturing Battery Grids

Willmore, C. B., 2,564,044, Aluminum-Magnesium Casting Alloys

Duddy, J. C., 2,564,397, Microporous Diaphragms and Method of Making the Same

Mullen, J. B., 2,564,495, Deferred Action Primary Battery

Johnson, H. L., and Stuart, A. P., 2,564,534, Polychlorinated Vinylcyclohexene and Its Use as Insecticide

August 21, 1951

Arent, A., 2,564,661, Steel Plating Method

Wallace, E. H., 2,564,823, Electropolish Interrupter

Ferrand, L., 2,564,837, Cell for the Electrolytic Production of Aluminum

Hodge, A. W., 2,564,844, Copper-Iron-Chromium Alloy

Thompson, J. S., 2,564,864, Method of and Solution for Increasing Resistance to Corrosion

Black, H. R., 2,564,950, Glass-To-Metal Seal and Composition Thereof

Smith, E. K., 2,565,004, Method of Forming Oxide Coating on Tantalum Electrodes

Warner, J., 2,565,010, Combined Battery Filling Cap and Plug

Volochine, T., 2,565,105, Thermoelectric Radiation Receiver

Wernlund, C. J., 2,565,189, Electropolishing Steel

Payson, P., 2,565,264, Hardenable Alloy Steels Resistant to Softening at Elevated Temperatures

Shuler, C., Godfrey, C. J., and Medlar, L. A., 2,565,273, Battery Charger

Amico, S. F., 2,556,338, Germanium Crystals

August 28, 1951

Driver, D. L. A., 2,565,483, Process for Manufacturing Selenium Cells

Ingram, M., 2,565,501, Salinity Indicator System

Brown, R. H., 2,565,544, Cathodic Protection and Underground Metallic Structure Embodying the Same

Zachlin, A. C., 2,565,674, Storage Battery

Gittings, D. O., 2,565,768, Aluminum Coating of Ferrous Metal and Resulting Product

Beanblossom, W. S., 2,566,052, Process for Photochemical Chlorination of Hydrocarbons

Loverde, A., and Beanblossom, W. S., 2,566,065, Processes for Photochemical Chlorination of Hydrocarbons

Zert, K., 2,566,105, Method of Manufacturing Carbon Depolarization Bodies for Atmospheric Oxygen Elements

Bloch, R., 2,566,114, Electric Cell

Bounds, A. M., 2,566,115, Alloy for Cathode Element

September 4, 1951

Benning, A. F., and Richards, M. K., Application 601,116, Electrode Assemblies

Brewer, A. K., 2,566,308, Process and Apparatus for the Electrochemical Separation of Chemicals by Ion Migration

Mager, E. L., 2,566,349, Electroluminescent Lamp

Symmes, W., 2,566,467, Stripping Cathode

Taylerson, E. S., 2,566,468, Method of Treating Electrolytic Coatings

Rabbitts, A. T., 2,566,676, Electrodeposition Apparatus

Hook, G. C., 2,566,887, Corrosion Inhibitor

Ruscetta, R. A., 2,566,908, Electrolytic Capacitor

Malowan, J. E., 2,567,156, Corrosion Inhibitor for Concentrated Phosphoric Acid

September 11, 1951

Blake, W. O., 2,567,542, Battery Breaking Machine

Kaplan, M. L., 2,567,713, Light Filter for Black and White and Color Television Receivers

Kaplan, M. L., 2,567,714, Cathode-Ray Tube

Head, R. B., 2,567,769, Alkaline Earth Oxysulfide Phosphor

Pippin, C. A., Robinson, M. O., and Bennett, W. R., 2,567,855, Rapid-Wetting Bentonite-Calcium Sulfate Backfill for Cathodic Protection

De Ment, J., 2,567,877, Electrochemical Bonding of Aluminum with Other Materials

September 18, 1951

Green, D. F., Mallet, N. P., and Briscoe, J. M., 2,567,934, Process of Electrodepositing an Alloy of Lead and Indium

Scaff, J. H., and Theuerer, H. C., 2,567,970, Semiconductor Comprising Silicon and Method of Making It

Lee, G. L., and Eash, J. T., 2,568,013, Cast Graphitic Nickel Alloy and Method of Making Same

Eash, J. T., and Lee, G. L., 2,568,014, Graphitic Nickel Tin Alloy and Method of Making Same

Willmore, C. B., 2,568,179, Aluminum Base Alloys

Willmore, C. B., 2,568,180, Aluminum Base Alloys

Martinet, N., 2,568,199, Method and Apparatus for Testing Papers and the Like

Bennett, F. C., 2,568,578, Electrically Heated Transfer Pipe

Robinson, H. A., 2,568,594, Galvanic Anode Assembly

September 25, 1951

Beck, A. H. W., 2,568,705, Nonsputtering Cathode for Electron Discharge Devices

von Hippel, A., and Bloom, M. C., 2,568,780, Rectifier Manufacturing Process and Products Obtained Thereby

Benning, A. F., and Richards, M. K., 2,568,844, Process and Apparatus for the Electrolytic Production of Fluorine

Spruance, F. P. Jr., 2,568,936, Method of Improving the Resistance to Corrosion and Abrasion of Certain Coated Aluminum Surfaces

Heyrovsky, J., 2,569,100, Apparatus for Electrolytic Investigation of Solutions

Roscoe, J. W., 2,569,116, Static Charge Removal Device

Gelardin, B., 2,569,159, Gas Permeable Coating for Dry Cell Flashlight Batteries

Osborne, S. G., and Mitchell, A., 2,569,329, Operation in Electrolytic Alkali Chlorine Cells

Willihnganz, E., 2,569,361, Electrochemical Cell Diaphragm

Bradner, D. B., Stoddard, W. B., Jr., and Blickensderfer, P. S., 2,569,368, Joining Metal Parts

October 2, 1951

Chester, A. E., and Schram, I. H. Jr., 2,569,453, Vitreous Enamel Base Stock, Vitreous Enameled Articles and Method

Leontis, T. E., 2,569,477, Magnesium Alloy

Otto, E. M., 2,569,491, Dry Cell Composition

Reading, H. J., 2,569,577, Method of and Apparatus for Electroplating

Rieger, E. W., 2,569,578, Apparatus for Electrocoating Striplike Material

La Lande, W. A. Jr., Aeugle, M. E., and Molyneux, G., 2,569,677, Photochemical Production of Benzene Hexachloride

Lyon, D. W., 2,569,939, Infrared Phosphors

Lyon, D. W., 2,569,940, Infrared Phosphors

Calkin, F. G., 2,570,096, Facsimile Wet Electrolytic Recording

Heine, G. F., 2,570,123, Device for Facilitating the Checking of Storage Batteries

Lyon, D. W., 2,570,136, Infrared Phosphors

Weber, C. F., 2,570,174, Metal Cleaning and Plating Process

October 9, 1951

Bohnet, W. J., and Bagley, G. D., 2,570,311, Electric Induction Furnace

Gorin, E., 2,570,543, Conversion of Carbon to Electrical Energy
Honey, E. M. O., and Hardy, C. R., 2,570,677, Battery Separator
Bain, F. F., and Broun, O., 2,570,748, Wire Drawing Apparatus
Robinson, H. A., and Humble, H. A., 2,571,062, Sacrificial Anode System for Protecting Metals in Sea Water

October 16, 1951

Lord, F. Le B., 2,571,145, Battery Terminal Connector
Huebotter, E. E., 2,571,247, Electrodialytic Treatment of Well-Drilling Fluids
Rooney, J. T., 2,571,488, Thickness Measuring Device
Leland, G. H., 2,571,588, Alternating-Current Rectifier of the Selenium Type
Ruben, S., 2,571,616, Electric Current Producing Cell
Ford, W. D., 2,571,700, Method of Coating Thermocouples
Gray, A. N., 2,571,709, Apparatus for Electroplating Articles
Lewis, R. W., and Linton, A., 2,571,732, Primary Electric Cell
Perkins, F., 2,571,754, Process of Prolonging the Life of a Storage Battery
Kendall, T. L., 2,571,893, Submersible Vent Cap
Lawlor, F. E., 2,571,901, Chlorinating Process
Longini, R. L., 2,571,905, Zinc Sulfide X-Ray Phosphors
Neumann, G., and Gottesmann, U., 2,571,927, Electrolytic Cell and, in Particular, Alkaline Cell
Swartout, J. A., 2,571,965, Process for Production of Radioactive Iron
Rupp, J. L., 2,571,988, Storage Battery

October 23, 1951

Berl, L., 2,572,002, Photochemical Formation of Benzene Hexachloride
Ellis, G. B., 2,572,017, Dry Battery Cell
von Hippel, A., Bloom, M. C., and Schulman, J. H., 2,572,079, Radiation-Sensitive Cells and Method of Making Same
Valentine, K. B., 2,572,219, Method of Processing Electroplated Spring Steel Parts
Cooper, H. S., 2,572,248, Electrolytic Method of Making Boron
Cooper, H. S., 2,572,249, Electrolytic Production of Elemental Boron
Zimmerman, H. M., and Cahoon, N. C., 2,572,296, Primary Cell and Battery and Method of Making Same
Duddy, J. C., 2,572,324, Storage Battery Construction

LITERATURE FROM INDUSTRY

ACID-PROOF TANTALUM EQUIPMENT. A 28-page booklet on the chemical and physical properties of tantalum gives detailed engineering descriptions of single and multiple tube bayonet heaters, coils, heat exchangers, condensers, hydrochloric acid absorbers, instrument protection, tubing and fittings. 72 illustrations and 4 tables. Fansteel Metallurgical Corp. P-1

MEASURING EQUIPMENT. A new 80-page catalog (GEC-1016) summarizes testing and measuring equipment for laboratory and production line use. A ready reference to the apparatus available, it contains more than 150 photographs and diagrams, and describes the uses, features, and prices of 130 testing and measuring equipments. General Electric Co. P-2

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The Electrochemical Society

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Address all correspondence to the Editor, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 235 W. 102nd St., New York 25, N. Y.

FORM

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½–4 cm (1–1½ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

Drawings will be reduced to column width, 8 cm (3⅛ in.), and after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

Captions for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40,** 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1,** p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for $Zn \rightarrow Zn^{++} + 2e$ is negative; for $Cu \rightarrow Cu^{++} + 2e$, positive.

ABBREVIATIONS

Abbreviations should conform with the American Standards Association's list of "Abbreviations for Scientific and Engineering Terms."

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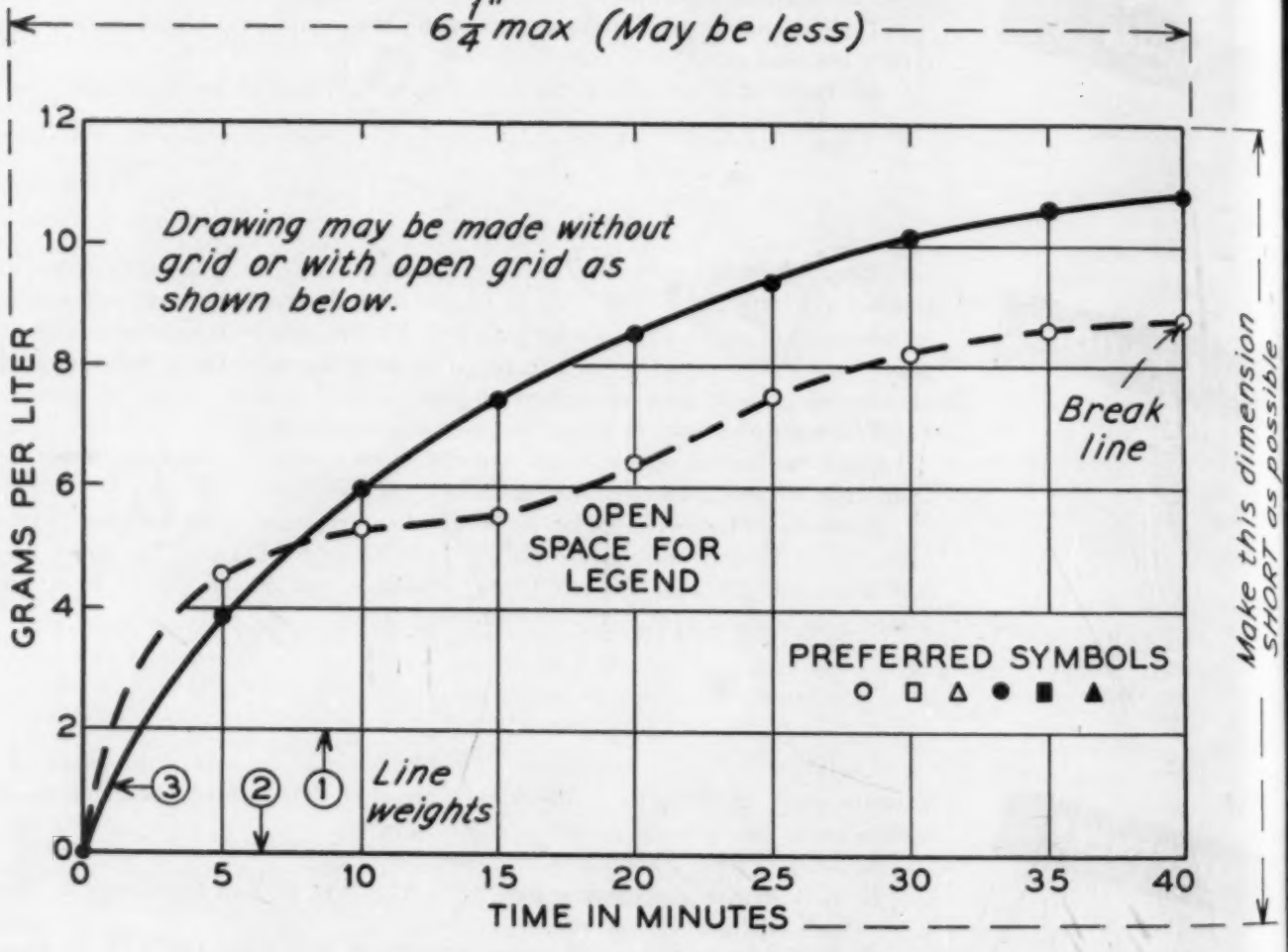
Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.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Editorial

More Electrodeposition Research

ON THE Golden Anniversary of The Electrochemical Society, it is a source of considerable gratification to those who are engaged in electrodeposition to look back on fifty years of remarkable progress in their chosen field. As members of The Electrochemical Society they can derive an additional measure of satisfaction from the knowledge that their Society has made many notable contributions to progress in electrodeposition. Many writers have observed that although activities in electroplating were instituted about one hundred years ago, it has only been during the past fifty years that the techniques in this field have progressed from an empirical art to a scientifically controlled process. The haphazard methods and unpredictable results of earlier decades have been supplanted by physical and chemical controls which lead to the production of deposits that meet widely-adopted specifications. Although The Electrochemical Society, composed as it is of those who are interested primarily in fundamental knowledge, has not participated in the formulation of industrial specifications, the contributions which its members have made to the science of electroplating have assisted greatly in making it possible for practitioners to produce deposits which meet specifications.

It is true, also, that there have appeared on the pages of the Society's publications a great many papers and discussions which have contained the original and basic information upon which many of the modern electroplating processes depend. When, in 1940, the Electrodeposition Division undertook the preparation and publication of "Modern Electroplating," it made a contribution whose importance can be judged by the extensive sale which the volume has enjoyed.

Although the occasion of an anniversary is properly a time for the summarization of accomplishments, it should serve equally well as a time for assessment of failures and a survey of what should be done in the future. In this connection we cannot help but regret the lack of progress in studies on the actual process of electrodeposition. It is true that we have learned a great deal about how to control the electroplating operation, but we have accomplished all of this very largely in an empirical manner. Nothing has been based upon deductions stemming from a *comprehensive* theory of the plating process itself. As a matter of fact, when one tries to describe how an ion is

(*Continued on next page*)

transferred from the plating bath to the lattice structure of the cathode one can speak only in the most general terms—terms which in no way give a clear picture of what is actually happening. It is evident to anyone who is curious as to the exact nature of the electrodeposition process that an immense amount of work remains to be done in this field. Such work will be valuable in directions other than the mere satisfaction of scientific curiosity. It is becoming increasingly apparent that significant progress in practical plating is now developiug at a slower rate than a few years ago. It would appear that the time of progress based upon empirical experimentation is rapidly coming to a close, and that further significant advances can be made only when the fundamentals of the plating processes are more completely understood than at present.

There is no reason why the future of electroplating should not be brighter than its past. There are ever increasing uses for plated metals as protective and decorative coatings, and there appears to be every indication that allied fields such as electroforming, electrowinning, and electrorefining will enjoy increasing applications. Perhaps at least one of these fields should be examined a little closer. Although electroforming has enjoyed extensive use in the fields of electrotyping and the manufacture of phonograph records it is only in the last few years that applications of this technique have extensively invaded other fields of manufacture. Perhaps one of the reasons why electroforming has not been extensively used is the lack of fundamental information on the nature of the process and the properties of the deposited metal. Metals which have been electroplated for protective and decorative purposes have been evaluated largely on the basis of cnly two criteria, appearance and corrosion resistance. Electroformed metals which arc to be used for structural and engineering purposes must not only meet many additional criteria of a physical and mechanical nature, but it is also necessary that these properties be consistently produced. The latter is an extremely important point and it is surely true that a thorough understanding of the fundamental nature of the plating process should assist greatly in designing processes which will consistently yield metal having the desired physical and mechanical properties.

The members of The Electrochemical Society include many investigators who are capable of significant attacks upon the many unsolved problems of electrodeposition. Let us hope that they will accept the challenge of the future in a manner commensurate with their accomplishments of the past.

—Harold J. Read

Fiftieth Anniversary

FIFTY YEARS OF ELECTRODEPOSITION

*William Blum**

Introduction

In certain respects it is almost as difficult to summarize the past as to predict the future. The former task requires not only some knowledge of what has happened in a specific field of science or industry, but also the ability to decide which developments are most significant. Such a selection may involve predictions, because it usually takes years for a new discovery or invention to find extensive applications, from which its importance may be evaluated. Hence, an historian must in some degree also be a prophet.

In the following effort to summarize the progress made in the last fifty years in the electrodeposition of metals, no effort will be made to discuss details or to give literature references. Instead, the purpose will be to present a "bird's-eye view" of electrodeposition in 1902 and in 1952. I hope that there will not be too much astigmatism in the eye of the "bird"! I was engaged in studies on electroanalysis as a student at the University of Pennsylvania in 1902 when I attended the first meeting of The Electrochemical Society. Hence, my scientific career is practically coincident with that of the Society.

General Principles

In the long run, the progress in any field of science or industry may best be gaged by the advancement in fundamental knowledge in that field, even though it is entirely possible for an industry to develop and expand for a limited period upon an entirely empirical basis. The large number of papers published since 1902 on such fundamentals of electrodeposition as polarization, overvoltage, addition agents, and the stress, structure, composition, and properties of electrodeposits is ample evidence that these subjects have not been neglected. In spite of these researches, however, it may be safely stated that there is today no theory of the mechanism of electrodeposition that will even approximately explain existing knowledge, much less permit predictions of the behavior of new or untried systems. The great advances that have been made in electrodeposition are therefore largely empirical.

Obstacles to progress in this direction are (*a*) the present gap in our knowledge of the constitution of the strong solutions commonly used in electrodeposition in spite of the Debye-Hückel theory and its modifications, and (*b*) the lack of persons with both sufficient knowledge of the physical chemistry of solutions and sufficient interest in electrodeposition to bridge the gap between science and this industry. At The Electrochemical Society meeting twenty-five years ago, an excellent summation of the knowledge of solutions was made by P. Debye, V. K. LaMer, T. J. Webb, G. Scatchard, and H. S. Harned, under the chairmanship of H. S. Taylor. We need more such symposia, and also more persons to interpret and use the information in studies on electrodeposition.

I hope that the above remarks will not be considered as a criticism of the many persons who have devoted their efforts to increasing our basic knowledge of electrolysis. On the contrary, it is an appreciation of the value of their efforts that leads me to appeal for more interest in, support of, and utilization of fundamental studies on electrodeposition. Unfortunately the present justifiable emphasis on practical results that may be used immediately by industry or the defense agencies frequently precludes those basic studies that may ultimately prove more productive. It is to be hoped that through such agencies as the National Science Foundation greater support can be given to basic research.

Electroanalysis

One of the phases of electrodeposition to which most chemistry students are exposed is electroanalysis, upon which many papers were published by E. F. Smith and A. Classen before 1902. Since that time relatively few new electrolytic determinations or separations have been published. H. J. S. Sand early proposed the use of a controlled potential for separating metals, a procedure that was applied in recent years for the separation of uranium from other metals. A modification, known as "internal electrolysis," in which a desired potential is maintained by using a soluble anode of a more base metal such as zinc or magnesium, has found limited application.

Electrolytic determinations of copper, nickel (+ cobalt), and zinc have been used extensively in works control, but other metals are not generally so determined, usually because of interfering elements.

Electrowinning

The electrowinning of zinc, by extraction of the ores and electrolysis of the solution with insoluble anodes, was studied during the latter part of the nineteenth century, but did not come into large-scale operation until the period from 1915 to 1925. Since then its use has expanded rapidly, so that in 1948 about 40 per cent of the U.S. production of zinc was electrolytic. The principal factor in this rapid development was the realization that zinc can be deposited with high efficiency from strongly acid baths if all metallic impurities are scrupulously removed. The Tainton process, used for the production of "Bethanized" steel wire, is an example of the electrowinning of zinc to yield in one operation plated protective coatings.

Electrorefining

Over 80 per cent of the copper produced in the U.S. is refined electrolytically. The methods, solutions, and equip-

* National Bureau of Standards, Washington, D. C. (Retired on December 31, 1951).

ment used are essentially the same as those employed before 1900, with only those minor but important changes that depend on increase in knowledge and experience, and on the improvement of electrical generators and equipment.

Electrolytic lead refining was developed by Betts in the first quarter of this century and was used successfully in British Columbia. So far as can be learned, it has been applied commercially in the U.S. in only one plant, the U.S. Lead Refining Company of East Chicago.

Electrolytic refining of nickel in Canada has been developed during the past fifty years, and in 1948 it accounted for more than 90 per cent of the total nickel output of that country. This method permits recovery of the platinum metals. Somewhat less than 1 per cent of the total nickel used in the U.S.A. is recovered from electrolytic copper refining plants.

The present unsettled international situation, with the resulting shortages of metals such as nickel, tin, and copper, makes it impossible to predict developments in the electrolytic production of these metals. The fact that electrowinning may be applied to low-grade ores, and that electrorefining fosters the recovery of byproduct metals, may well increase the use of these electrolytic processes.

Electroplating

In 1927 G. B. Hogaboom concluded his paper on "Twenty-five Years of Electroplating" with the prediction that "At the Golden Jubilee of this Society the work of the past twenty-five years will seem like that of a Lilliputian." In spite of the real and far reaching advances in electroplating there has been no "revolution" in that industry. Probably the most significant, and certainly the most visible, change in electroplating has been the application of chromium for decorative plating. In 1927 this was just coming into use; today practically all plated metal parts on automobiles, electric appliances, and household utensils have a final thin layer of chromium to resist tarnish.

Another significant development is the widespread use of "bright" nickel plating, which eliminates most of the buffing and saves nickel. In spite of the success in achieving this objective, it must be admitted that most of the addition agents and brighteners are selected empirically. Far more research is required to establish the functions of specific groups in organic compounds now added to nickel or other plating baths.

More significant is the improvement in the quality of plated coatings. In 1902 there was little control of the plating operations and coating thickness. Consequently the quality was erratic. The advent and rapid growth of the automobile industry since 1900 soon led to a demand for plated coatings of uniformly high quality. To define the requirements extensive exposure tests of plated coatings were conducted through the cooperation of the American Electroplaters' Society, the American Society for Testing Materials, and the National Bureau of Standards. On the basis of these and other observations, numerous "type" specifications were promulgated, which are still in the process of improvement and refinement.

Because these studies and experience showed the importance of the thickness of the coatings, especially the minimum thickness, rapid, reliable methods for measuring the local thickness were developed, including the dropping test, jet, and magnetic methods.

Efforts to develop quantitative inspection tests for adhesion were less successful. The "nodule" method of Brenner is ingenious and may be adapted to routine inspection. The Ollard and Jacquet methods require specially prepared specimens and are hence not applicable for inspection.

Because many applications of electroplating and electroforming depend on the physical properties of the deposits, these have been critically studied. It is not yet fully appreciated, especially by design engineers, that it is possible by electrodeposition to produce deposits of the same metal with a wide range of physical properties. Recent studies on nickel deposits, conducted at the National Bureau of Standards in cooperation with the American Electroplaters' Society, include values for a wide diversity of properties, and their relation to the composition and structure of the deposits and the conditions of deposition.

Another advance is in the realization that the properties of electrodeposits may depend on the presence of small amounts of impurities such as hydrogen, oxygen, sulfur, chlorine, and carbon. Far more study is required to define the source, form, and location of these inclusions.

There has not been a great change in the types of plating baths. Those for bright nickel, referred to above, are usually modifications of the Watts bath. The chromic acid bath containing sulfate is still in general use, in some cases with an excess of a sparingly soluble compound, which serves to maintain the content of sulfate or other "catalyst." Cyanide baths are still extensively used for copper, silver, gold, zinc, and cadmium, with at most minor changes in composition.

The scarcity of tin in World War II (and at present) promoted a great expansion of electrolytic tin plate, which can be applied much thinner, e.g., 0.00003 in. (0.5 lb per base box) than can the hot dipped tin, which is usually 0.00009 to 0.00012 in. thick (1.5 to 2 lb per base box). Both acid and alkaline tin solutions are used, the former including a cresol sulfonate bath and a chloride-fluoride bath; and the latter, sodium or potassium stannate baths. Fluoborate solutions, long used for tin and lead, have been adapted to a limited extent for copper and nickel deposition. Pyrophosphate solutions of copper and zinc have found limited applications.

Deposition of the platinum metals has received considerable study. Of these rhodium has found the most application, first on large searchlight reflectors, that have now been rendered nearly obsolete by radar, and more recently on electrical contacts.

Alloy deposition has received far more study than application. Brass plating is very extensively used, e.g., on hardware, and is still conducted on an essentially empirical basis. Lead-tin alloy deposits have been used to some extent, especially as a means of conserving tin in substitutes for terneplate. Gold alloy deposits are used to produce "colored" gold, such as green gold, rose gold, etc. Tin-zinc alloys and tin-nickel alloys have been developed too recently in England to permit their extensive application. Numerous papers have appeared on the deposition from aqueous solutions of alloys of tungsten or molybdenum with iron, nickel, or cobalt, but neither pure tungsten nor molybdenum has been produced from aqueous baths.

Before any alloy deposit warrants industrial application, it is necessary to show by experiment not simply that an alloy of the two metals can be produced but also that it has properties that are sufficiently different from those attainable with a single metal that the extra trouble of alloy deposition is warranted. Alloy deposition should receive far more exhaustive study, but it is not justifiable to assume that it is a panacea for all the ills of normal plating.

All available evidence indicates that it is not possible to

deposit from aqueous solutions the borderline elements such as molybdenum and tungsten (alloys of which can be deposited), or those more negative metals such as beryllium, aluminum, titanium, and zirconium. During recent years there has been a greatly increased interest in the possibility of depositing any of these metals in a pure form, with good physical properties. If this can be accomplished, there will be numerous applications in industrial and defense equipment. Hence, research on this subject is now being conducted in a number of laboratories, including studies with fused salts and with organic solutions. While, so far as known, the goals have not yet been reached, it is practically certain that the present intensive program will lead to the successful deposition of one or more of the unusual metals. I therefore venture the prediction that within the next twenty-five years electrodeposition of some of these metals from nonaqueous media will be commercially practiced, at least for special applications.

Electroforming

In 1924, the author coined the term electroforming to cover the production or reproduction of articles by electrodeposition. Of course such processes were in common use long before then; in fact, certain of the earliest applications of electrodeposition were in the reproduction of coins and medals.

By far the widest application of electroforming is in electrotyping, i.e., the reproduction of printing plates. This dates back to about 1839 when Jacobi, Spencer, and Jordan each reported their electrolytic reproduction of designs. By 1900 the electrotyping industry was well established, and copper and nickel solutions, similar to those now used, were generally employed. In the first quarter of this century the advances were principally in better knowledge and control of the baths and operations, together with improvements in mechanical equipment.

During the past decade a veritable revolution in electrotyping has been brought about by the substitution of plastic for the wax or lead molds previously used, and the substitution of chemically-reduced silver instead of graphite to render the surface conducting. As a consequence the plant and equipment, formerly covered with graphite dust, can be kept as clean and attractive as a drawing room.

Other applications of electroforming have been less constant and consistent. The production of thin sheet copper is successful, but the electroforming of tubes of copper or iron has not proved economical. Special shapes such as musical instruments, Pitot tubes, fountain pen caps, and certain military devices have been successfully electroformed. In the last decade there has been a renaissance of electroforming, and the industry is no longer a "will-o-the-wisp," as the author once called it.

It is hard to state in general terms the optimum fields for electroforming. It is not generally useful for producing a single article, as the expense for the mandrel and the necessity for trial runs may cost more than making the article by hand. Conversely, it is usually not efficient for making very large numbers of an article, e.g., millions of pieces, for which the high cost of stamping dies and presses can be readily absorbed. Purely as an illustration, electroforming should be considered for making from 10 to 10,000 reproductions, when high precision is required. Certainly the future of this field looks brighter than it did 50 years ago.

Future Progress

The very significant progress in various fields of electrodeposition during the past 50 years may be largely attributed to the activities of The Electrochemical Society, started in 1902, and the American Electroplaters' Society, founded in 1913. In England the Faraday Society (1903) and the Electrodepositors' Technical Society (1926) have served similar functions. The greatest value of these organizations probably lies, not in their publications, but in the promotion of the association of persons of different but related interests. Their committee activities have stimulated advances that could be made only by concerted effort.

The question may well be asked, "Why have an Electrochemical and an Electroplaters' Society?" The fact that their interests are complementary and not competitive may be shown by the large list of persons with membership in each organization. The most obvious distinction, viz., that The Electrochemical Society deals with principles and generalities and the Electroplaters' Society with plating practice, is no longer as sharp as formerly, because the electroplating industry is becoming more scientific, and the AES is conducting and supporting much fundamental research.

Nevertheless there is a distinction which should be emphasized and not obliterated. The Electrochemical Society may well organize meetings and symposia devoted largely to those fundamentals of electrochemistry that apply to all its branches, without emphasis on specific applications in industry. The Electroplaters' Society, in addition to publishing the advances in the art and science of electrodeposition, should strive more to interpret and apply the newest developments in physical and electrochemistry. With a sound coordination of the activities of these two organizations we may well look for greater progress in electrodeposition in the next 50 years than in the past.

THE ELECTRODEPOSITION DIVISION

*Frederick A. Lowenheim**

The Electrodeposition Division of The Electrochemical Society was organized in 1922 to "advance the theory and practice of Electrodeposition." Long before the formal organization of the Division, however, the Society's meetings were making their contribution to these aims, by the presentation of papers and the holding of discussions concerning that broad field of electrochemistry which is embraced by the term Electrodeposition: the plating, refining, and winning of metals, and their analytical determination by electrochemical means. From the first convention of the Society on, this branch received a prominent share of attention.

The Electrochemical Society held its first meeting in April 1902, a year which also marked the appearance of the first volume of the *Transactions* of the Faraday Society. The importance of the emergent science of electrochemistry is emphasized by the inauguration one year later of two technical journals: *Electrochemical Industry* (now, after many changes of title, *Chemical Engineering*) and *Metal Industry* (now *Metal Finishing*). The American Electroplaters' Society had not yet been formed, but the idea for a national association of electroplaters was beginning to germinate in the minds of the leaders of the industry.

At early meetings of the Society, electrorefining and electrowinning figured more prominently than electroplating among the papers of general electrodeposition interest. Over the years the emphasis has shifted, reflecting the increasing attention which has been paid to plating by a growing number of qualified scientists who have naturally chosen the publications of The Electrochemical Society as the vehicle for their contributions; while at the same time practices in the field of refining and winning of metals have become somewhat stabilized so that there tends to be less new work to report.

Electrodeposition's Part in the Society

A brief survey of the TRANSACTIONS will serve to emphasize the part that electrodeposition has played in the affairs of the Society, and conversely to indicate the contribution that the Society has made to the art and science of electrodeposition. A detailed review would reveal that the outstanding leaders in the field have been regular contributors to the symposia and discussions.

In Volume I we note three papers: "The Electrical Reduction of Lead," "The Electrolytic Refining of Composite Metals," and "A Method of Electrolytic Production of Zinc from its Ores." Volume III reports "Notes on Modern Electrolytic Copper Refining," "Notes on the Composition of Electroplating Solutions," and "Notes on the Electrodeposition of Zinc." At the fourth meeting of the Society, W. D. Bancroft read a paper on "Electrolytic Copper Refining," of which it was said in discussion that "This paper is of interest, for it gives the views of a college professor on a practical process that was developed solely along practical lines." Volume V contains Addicks on "The Economic Balance in Electrolytic Copper Refining" and Burgess and Hambuechen on "Electrolytic Iron."

It is not the intent here to list all papers of electrodeposition interest which have appeared in the TRANSACTIONS of the Society; such a listing would serve no apparent purpose and would doubtless make rather boring reading. Enough has already been said to prove the point that the Society, from its inception, paid due regard to this field, and it will suffice to note some of the high spots as they appear in the TRANSACTIONS for succeeding years.

Bancroft's Axioms

In Volume VI (1904) appeared the historically interesting paper by Patten on the deposition of aluminum from ethyl bromide solutions, and one paper by Bancroft which elicited much discussion, "The Chemistry of Electroplating." The author introduced his subject by remarking that "a glance at the recent textbooks on electrochemistry will show how far we still are from any consistent theory of electroplating. The reason for this is to be found in our neglect of the chemistry involved." The paper was summarized by its author in a series of conclusions which came to be known as Bancroft's axioms of electroplating:

"1. A bad deposit is always due to the precipitation with the metal of some salt or nonmetal.

"2. Addition to the solution of anything which will dissolve this salt or nonmetal will tend to prevent its precipitation and to improve the quality of the deposit.

"3. Any beneficial action of a reducing agent is probably due to the removal from the solution of dissolved oxygen.

"4. A fine-grained deposit is favored by high current density and potential difference, by acidity and alkalinity, by low temperature, and by colloids.

"5. Solutions containing oxidizing agents appear to yield small crystals while larger crystals are obtained from solutions containing reducing agents.

"6. The adherence of deposits rests on the adhesion of the two metals."

The value of the paper was not unanimously admitted. One discusser said, "Professor Bancroft's paper, in my opinion, does not bring us any nearer a solution of the important question raised." But the chairman, Dr. Burgess, thought that "We ought to be thankful for a paper of this sort. . . . The electroplating industry is perhaps the oldest industrial application of our electrochemistry, but electrochemistry, at the present time, is in a most unsatisfactory condition as regards its literature."

Almost as valuable as the formal papers themselves, at these early meetings of the Society, were the discussions, the printed transcripts of which continue to provide interesting reading up to the present time even when the controversies involved have long since been resolved. Discussers were frank, often brutally so, and few holds were barred; and it cannot fail to fascinate the younger readers of today to witness, by proxy, the verbal battles between scientists whose names have in the intervening years become elevated to a position of high honor. Even while recognizing the inevitability of the development, we may regret the necessities which have caused the discussions at present-day meetings to appear tame and uninteresting by comparison.

Volume VII, of 1905, contains the historical paper by Carveth and Curry on Chromium and the Electrolysis of Chromic Acid. In Volume IX (1906) we find a paper by Dr. Isaac Adams, "the father of the nickel-plating industry,"

* Metal & Thermit Corporation, Rahway, New Jersey.

which tells the story of the early development of his process and which precipitated a controversy concerning allocation of proper credit for it; Burgess and Watts contributed a paper on the Microscopic Study of Electrodeposits; Curry on the Electrolytic Precipitation of Bronzes; and LeBlanc on Electrolytic Chromium. The last-named was highly controversial, the work of Carveth and his coworkers being particularly criticized. President Bancroft, in the chair, remarked that "The real solution from which to deposit chromium is not chrome alum nor chromium sulfate, it is chromic acid."

The electrometallurgy of zinc was the subject of several papers in succeeding volumes. In Volume XV, E. F. Kern discusses the Function of Addition Agents in Electrolytes; Tucker and Thomssen report the Deposition of Aluminum from Aqueous Solutions; and Patten and Mott write on the Electrodeposition of Some Metals from Acetone Solution. Volume XVII (1910) contains Mathers' paper on the Electrodeposition of Lead from Perchlorate Solutions.

Closer Relations with Electroplaters

A paper which stirred up a great deal of discussion was G. B. Hogaboom's, in Volume XIX, on Some Unsolved Problems in Electroplating. Mr. Hogaboom's paper was the harbinger of a long period of friendly competition coupled with cooperation between The Electrochemical Society and the Electroplaters' Society, and as such it is worth quoting as an indication of the need which existed, and still exists, for understanding and co-operation between the practical plater and the scientist. "There has existed for such a long time a separation of the practical plater and the electrochemist that ... it is hoped that the practical end of electroplating, as represented by the National Electroplaters' Association*, and the scientific end as represented by this Society, will be brought into a closer relation. As is well known, electroplating was the beginning of the science of electrochemistry, but it has lingered by the wayside and been neglected as a science, and today the unsolved problems are many.

"Electroplating has been looked upon more as a trade than a science, and it is only during recent years that much study has been given to it by scientists, and that attention has been directed more to the electrolytic refining of metals than to the deposition of metal for decorative purposes. The solutions published by Roseleur in 1854 have been improved upon but little, and those who have published treatises upon the subject often give only a repetition of his formulas. Nickel plating, as invented by Dr. I. Adams, is probably the only exception.

"The field is broad, but its development has been left to the practical man, guided only by 'rule of the thumb.' An electrochemist in the plating room of a factory is so rare that it probably can be said without fear of contradiction that they can be counted on the fingers of one's hands. The need today is mutual assistance in solving these problems and developing new ideas."

That this plea for mutual understanding and co-operation did not go unheeded is evidenced by Volume XXIII of the TRANSACTIONS (1913), which can in a sense be called the first edition of "Modern Electroplating." Here is a partial table of contents of this volume:

The Electrodeposition of Metals—W. L. Miller
The Electrodeposition of Gold and Silver—F. C. Frary
The Electrodeposition of Cobalt and Nickel—O. P. Watts
The Electrodeposition of Lead—F. C. Mathers
The Electrodeposition of Tin—E. F. Kern
The Electrodeposition of Copper—C. W. Bennett
The Electrodeposition of Brass and Bronze—C. W. Bennett
Discussion on the Electrodeposition of Metals

The Proceedings note that "the members of the American Electroplaters' Society were invited to attend the Symposium and take part in the discussion, and a number of their members were present." The Proceedings also reveal that "On motion of Dr. W. D. Bancroft the following members were appointed a committee to co-operate with a similar committee of the American Electroplaters' Society in preparing a report on the whole subject of electroplating: W. D. Bancroft, Chas. H. Proctor, and Geo. B. Hogaboom, with power to add to their number." Later the following were were added to this committee: C. W. Bennett, F. C. Frary, F. A. Lidbury, and F C. Mathers.

This symposium on the science of electroplating was of great historical significance for several reasons. So far as the present author is aware, it was the first attempt to apply systematic academic effort to the art of the plater; it marked the first step in a long and fruitful series of co-operative programs on the part of the scientific and the technical men interested in electrodeposition; and furthermore, this volume of the TRANSACTIONS remains of considerable importance for bibliographic purposes: there is no better starting point for searching the old literature on electroplating. Mr. Charles H. Proctor, in opening the discussion of the symposium, said:

"As one of your individual members and a representative of the American Electroplaters' Society, I can assure you it gives me great pleasure to meet with you in this your first Symposium on electroplating. I believe this will be a red letter day in the history of the electrodeposition of metals, because from this day hence we can rely upon the electrochemist to participate with us in bringing the art to a higher level, and a day when men of theory can join hands with the practical man who has toiled for years and, with dogged indifference to his surroundings, has brought the art of electroplating to its present standard in the commercial world."

In reading the discussions which followed the presentation of the individual papers, the modern reader is once more struck by the vitality and frankness evidenced. There can be little doubt that Mr. Hogaboom was right when he said, in discussion, "This day marks an epoch in the history of electroplating in this country."

Volume XXVI (1914) was once more almost entirely devoted to electrodeposition. In the Proceedings of Volume XXVII we read that "the report of the Committee on Cooperation with the American Electroplaters' Society, communicated by Chairman Bancroft, was received and the Committee continued. It reads as follows: 'F. C. Mathers has studied the behavior of many nickel baths and silver baths but is not yet ready to report. In the nickel baths he finds that the effect of boric acid is specific and is not due to its being a weak acid. F. C. Frary has measured single potentials and is not ready to report.' "

Technical Committees Formed

This same year marked the formation of Technical Committees of the Society, the forerunners of the present Divisions. There was a large Committee on Electrometallurgy, with a different member for each metal, as follows: Chairman, J. W. Richards; Refining Subcommittee, Copper—R. W. Deacon; Lead—William Thum; Zinc—C. A. Hansen; Iron—

* Later the American Electroplaters' Society.

C. F. Burgess; Silver—C. H. Aldrich; Gold—W. H. Peirce; Miscellaneous—A. G. Betts. The Committee on Electro-Plating (which had not yet lost its hyphen) consisted of F. C. Frary, chairman; E. F. Weston and G. B. Hogaboom. And one afternoon session of the meeting was a joint meeting with the American Electroplaters' Society.

At the twenty-ninth meeting, Hogaboom presented a second paper on unsolved problems of the electroplater; Mathers, Stuart, and Sturdevant, as the Committee already mentioned, gave their report on Nickel Plating, and O. P. Watts contributed a paper on Rapid Nickel Plating. There were other papers of electrodeposition interest; the pattern of at least one meeting a year largely devoted to electrodeposition was beginning to be set.

The number of papers on electrodeposition begins to increase markedly during this period, and it is obviously impractical to try to note even a fraction of them. The first World War created a great demand for more knowledge of the electrodeposition process, which was reflected in the number of contributions published. G. B. Hogaboom became chairman of the Technical Committee on Electroplating in 1917, succeeding F. C. Frary. In 1918 Blum presented a paper on "Military Applications of Electroplating" in which it is stated that "At the present time, the principal applications of plating upon military supplies are zinc, black nickel, and lead. A considerable amount of copper and nickel plating, and some tin plating, is still required, though in general these methods are being largely superseded by zinc plating." In 1919 Blum contributed an important paper on "Factors Governing the Structure of Electrodeposited Metals," and with co-workers also reported on Lead Plating from Fluoborate Solutions. In 1920 appeared Sargent's report on Electrolytic Chromium, in which it was shown that "very good deposits of chromium were obtained from chromic acid solutions containing small amounts of chromic sulfate .... The chromium plating is extremely resistant to corrosion by air, moisture, and many chemicals."

The Division and Its Purpose

This period in our history of Electrodeposition and the Society came to an end in 1921; for in Volume 40 we read that the Board of Directors have authorized the formation of an Electrodeposition Division; its first officers were reported in Volume 41 as G. B. Hogaboom, chairman; Chas. S. Witherell, vice-chairman, and William Blum, secretary-treasurer. Directors (an office since discontinued) were L. Addicks, F. C. Mathers, E. F. Kern, and O. P. Watts. The by-laws of the Division, promulgated in January 1922, read in part:

"This Division is organized to advance the theory and practice of Electrodeposition. To this end, through meetings and papers, it will especially aim to stimulate discussion of the various technical phases of the subject, including:

"1. Electrodeposition of metals, alloys, and metal oxides.
"2. Applications of electrodeposition in electroplating, electrotyping, electrorefining, and electroanalysis.
"3. Properties directly related to electrolysis, such as conductivity, polarization, and electrode potentials.
"4. Methods of analysis developed especially with reference to electrodeposition.
"5. The structure and properties of anodes and of electrodeposited metals.
"6. The design and operation of equipment for electrodeposition."

Remaining provisions of the by-laws had to do with officers and their duties, etc., and since they have a standard form they need not be quoted here. These by-laws have been amended several times, most recently on June 21, 1950; declaration of purpose has evolved until it now reads:

"Article II: Purpose: To encourage education, training, research, and publication in the fields of electroplating, electroforming, electrorefining, and electrowinning and to cooperate with other sections of The Electrochemical Society in the extension of scientific knowledge in the field of electrochemistry."

"Modern Electroplating"

After the formation of the Division, papers on electrodeposition subjects became more and more numerous, and no attempt will be made to list any of them. Well-integrated symposia on electrodeposition were scheduled every few years, with miscellaneous papers of all grades of importance and merit appearing in nearly every volume. In 1924 (Vol. 45) was held the symposium on Recent Progress in Electrodeposition; and every volume up to 78 (for 1940) reports a symposium on electrodeposition containing usually up to ten or twelve papers. The majority of these papers are on electroplating, but the subjects of refining and winning are not neglected. Of particular note is the long and important series of papers in Volume 59. The first volume to lack a symposium on electrodeposition is Volume 79, for 1941, but this was merely the calm before the deluge, for Volume 80, of course, contains the symposium on "Modern Electroplating," which represented the most ambitious attempt at gathering an integrated and definitive series of papers which the Division, and possibly the Society, had yet attempted. Recognized experts in their respective fields contributed authoritative reviews of the best practice in electrodepositing all of the commercially important plating metals. This symposium, reprinted as the book "Modern Electroplating" and published by the Society, became a best-seller in its field, and is still, ten years later, one of the two or three standard texts for the electrodepositor.

At about the same time the Division adopted the policy of confining its sessions to one a year, and with a few minor exceptions this practice has persisted: papers of electrodeposition interest are now scheduled where possible at fall meetings only, and they will be found in even-numbered volumes of the TRANSACTIONS from 80 to 96. After Volume 96 the publication policy of the Society was changed; with the issuance of the monthly JOURNAL the concentration of published papers into one volume is no longer possible. However, it remains true that oral presentation at meetings is confined in general to the fall, or even-numbered, meetings.

In addition to the regular annual sessions, two recent symposia are worthy of note: Modern Trends in Electroplating, Volume 82, and Strip Steel and Wire Plating, Volume 84.

The major activity of the Electrodeposition Division at this writing is the preparation of a Second Edition of "Modern Electroplating." Under the editorship of Dr. Allen G. Gray, an editorial advisory board and a distinguished panel of contributing authors have undertaken to revise and bring up to date this valuable book, and it is hoped that the Second Edition, which will be the first in the series of Electrochemical Society Monographs, will be a worthy successor to the original. In most instances the original authors have undertaken to revise their own chapters; in some cases new authors have been found. New chapters have been added reflecting the widening horizons of electroplating.

In winding up this short survey of the Society's contribution to the field of Electrodeposition, and more particularly

the activities of the Electrodeposition Division, it may be appropriate to seek the answers to two questions: Is The Electrochemical Society truly important to progress in this field, and has the Electrodeposition Division fulfilled a genuine function in the affairs of the Society?

The answer to the first question should be obvious. The short survey of papers which the Society has published should convince anyone that the Society's TRANSACTIONS have been the preferred medium for the publications of the leaders in the field, and that many of the most important advances in electroplating and allied arts have been first announced at its conventions. This is not to deny the importance of such organizations as the American Electroplaters' Society; there is room in a field as large as this for two organizations, which though they overlap do not coincide in their interests. The pleas of some of the founders of the Electroplaters', like Proctor and Hogaboom, for better co-operation between the electrochemist and the practical plater, have been answered to a large extent by the existence side by side of the two organizations with some duplication of membership and activities. It is only through progress in the fundamentals that major advances in practice will result, and The Electrochemical Society, representing those whose interests lie along fundamental lines, will remain of great significance to progress in Electrodeposition.

The Electrodeposition Division has justified itself in the affairs of the Society by arranging symposia which have attracted the interest of workers in the field and have in many cases convinced them of the desirability of membership in the Society. The Division remains the largest single group in the Society, and it may be said that Electrodeposition, in all its branches, is the backbone of the organization. In point of age, the Division is second, being outdone only by the Electrothermic Division.

There can be little doubt that the finest monument, so far, to the efforts of the Division as such is the 1941 volume on "Modern Electroplating," which has brought credit, and cash, to the Society and has served the needs of a generation of electrochemists and practical platers for definitive, reliable knowledge about plating processes. It is hoped that the forthcoming Second Edition will outshine even this achievement; and this might be an appropriate place to remark that few organizations, scientific or otherwise, could have commanded the unselfish and entirely unpaid devotion of so many outstanding experts, both editors and contributors, as have given of their time and talents in these enterprises. These books, and others sponsored by other Divisions, reflect the fact that, in some subtle way, The Electrochemical Society evokes in its members an esprit de corps which gives us confidence in its future.

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Current Affairs

GOLDEN ANNIVERSARY MEETING

Society Returns to Its Birthplace for 1952 Spring Convention

On April 3, 1902, a small group of scientists met at the Manufacturers Club in Philadelphia to organize the American Electrochemical Society. Now, fifty years later, although the Manufacturers Club no longer stands at Broad & Chestnut Streets and only nine of the original founders are still living, The Electrochemical Society, world-wide in scope with members in some forty countries, returns home to its birthplace to celebrate its Golden Anniversary at the Spring Meeting, May 4 to 8, 1952.

For more than a year the Convention Committee of the Philadelphia Section, under the chairmanship of Past President Hiram S. Lukens, has been working on arrangements for this meeting. Convention headquarters will be in the Benjamin Franklin Hotel, at 9th and Chestnut Streets, where all technical sessions and entertainment features will be held. As has been demonstrated in previous meetings of the Society, the facilities of the hotel are admirably adapted to the requirements of an Electrochemical Society convention. Room reservations should be made directly with the hotel management.

The tentative program calls for committee meetings and the opening of registration on Sunday, May 4th. Two technical sessions and a round-table discussion will be held concurrently on both the mornings and afternoons of May 5th, 6th, 7th and 8th. On Monday evening, May 5th, there will be a round-table discussion on the teaching of electrochemistry. The annual banquet will be held on Tuesday evening, May 6th, at which President Ralph M. Hunter will deliver the Presidential Address, a number of the Society prizes will be awarded, and Past President Lawrence Addicks, one of the founding members, will review briefly the early years of the organization.

Technical Sessions

The technical program will, of course, be a very important part of the meeting. Included will be sessions on Electric Insulation, Electrothermics, Instrumentation, Luminescence, Methods of Applying Phosphors, Rare Metals, and Theoretical Electrochemistry. In addition to these a number of round-table discussions of unusual interest are being planned. The exact schedule for all of these meetings will appear in a subsequent issue of the JOURNAL.

Luncheons and Plant Trips

Division luncheons will be held on May 5th and 7th, with a General Luncheon on May 6th, to which the ladies are invited.

Trips are being arranged to several of the local plants which will be of interest to electrochemists. The complete schedule for these will be published in the March issue.

Entertainment

A program of entertainment is being arranged which will give everyone an opportunity of renewing old friendships and of making new ones. Following the annual banquet on Tuesday evening, it is planned to hold a songfest, which will give the members a chance to demonstrate the versatility of their talents. On Wednesday evening, following a buffet supper, a unique entertainment has been planned. Full details cannot be announced at this time until the tentative program has been cleared with the F. B. I., the Treasury Department, the National Security Administration, and the Kefauver Committee.

Ladies' Program

With such a full schedule of technical sessions, it is important that the ladies attending the convention are not left to twiddle their thumbs while the menfolk are advancing the frontiers of science. With this in mind, the Ladies' Committee, under the chairmanship of Mrs. Russell P. Heuer, is preparing a well-rounded program for the feminine portion of the convention. Starting with a "Get-together Kaffee-Klatsch" on Monday morning, there will be trips to points of interest in old and new Philadelphia, to shopping and art centers, and a card party on Monday evening. On Wednesday, following a luncheon at one of the suburban country clubs, it is planned to visit the famous Bryn Athyn Cathedral and one or more of the outstanding private gardens in the vicinity. The Philadelphia suburbs are at their best during May and it is hoped that there will be a large attendance of ladies at the Spring Meeting to enjoy them.

Convention Committees

The Convention Committee is composed of the following members:

General Chairman, Hiram S. Lukens, University of Pennsylvania, Philadelphia 4; *Hotel Reservations*, Russell P. Heuer, General Refractories Co., 1520 Locust St., Philadelphia 2; *Meeting Accomodations*, Henry C. Miller, Pennsylvania Salt Mfg. Co., Wyndmoor, Pa.; *Registration*, Edgar L. Eckfeldt, Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia 44; *Finance*, Ernest G. Enck, Foote Mineral Co., 18 W. Chelten Ave., Philadelphia 44; *Entertainment*, Harry A. Alsentzer, University of Pennsylvania, Philadelphia 4; *Plant Visits*, Milton P. Barba, Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia 44; *Publicity*, Albert A. Ware, Ware Bros. Company, 317 N. Broad St., Philadelphia 7. *Ex-officio* members include the officers of the Philadelphia Section: John F. Gall, *Chairman*, Pennsylvania Salt Mfg. Co.; J. F. Hazel, *Vice-Chairman*, University

BENJAMIN FRANKLIN HOTEL
Headquarters for the Society's Golden Anniversary Meeting

of Pennsylvania; George F. Temple, *Treasurer*, Foote Mineral Co.; and *Past Chairmen* R. H. Cherry, Leeds & Northrup Co., and Arthur Osol, Philadelphia College of Pharmacy & Science.

Ladies' Committee

Mrs. Russell P. Heuer is chairman of the Ladies' Committee, and will be assisted by Mrs. Harry A. Alsentzer, Mrs. Milton P. Barba, Mrs. Edgar L. Eckfeldt, Mrs. Ernest G. Enck, Mrs. John F. Gall, Mrs. J. F. Hazel, Mrs. Hiram S. Lukens, Mrs. Henry C. Miller, and Mrs. George F. Temple.

Air Reduction Becomes Sustaining Member

The Society has the pleasure of welcoming the Air Reduction Company, Incorporated, 60 East 42nd Street, New York, New York, as a new sustaining member. This corporation is engaged in the production and sale of oxygen, acetylene, and the necessary apparatus and accessories for the oxyacetylene processes; also electric arc-welding apparatus and equipment; hydrogen, nitrogen, and rare gases; calcium carbide and acetylene for chemical uses; anesthetic and therapeutic gases, hospital and surgical equipment; and liquid and solid carbon dioxide.

Nearly 8,000 employees in more than 400 plants, warehouses, and sales offices, strategically located throughout the United States, serve almost every major industry through Airco's eleven operating divisions. This sales-service organization, together with four research and development laboratories, has been a leader in its field for many years.

Heading Air Reduction Company is President J. A. Hill. Dr. G. V. Slottman is director of research and engineering, and Dr. L. I. Gilbertson is administrative manager in charge of the Murray Hill Research Laboratories.

Dr. Frary Retires as Alcoa Research Director

Dr. Francis C. Frary, one of the nation's distinguished chemists and metallurgists, retired as Director of Research for Aluminum Company of America on January 1, 1952.

Dr. Frary was the founder of organized research in the aluminum industry. Joining Alcoa in December, 1918, he organized Aluminum Research Laboratories at New Kensington, Pennsylvania, and under his leadership it became one of the world's foremost industrial metallurgical research institutions. Among its notable achievements were the development of most of the modern aluminum-base alloys, the production of very pure (99.99%) aluminum by electrolytic refining, and the production of pure alumina—aluminum oxide—by electrothermal processes.

In his long career Dr. Frary lists many brilliant achievements and he has been the recipient of notable honors. Included in the latter are the Acheson Gold Medal and Prize, the Perkin Medal, the Gold Medal of the American Society for Metals, and the James Douglas Metallurgical Medal.

Dr. Frary is a past president of The Electrochemical Society and has been a member since 1907. He also holds membership in the leading metallurgical and chemical societies.

Electrochemical Society Prize Essay Contest

The second annual Prize Essay Contest sponsored by The Electrochemical Society has been announced. The subject selected is "The Electrochemical Nature of Corrosion" and two prizes will be awarded for the two best essays submitted. The first prize will be $100 plus a one-year membership in the Society; second prize will be $50, together with a one-year Society membership. The contest is open to undergraduate and graduate students. Essays, from 1000 to 2000 words, must be received at the Society offices by July 1, 1952. Winners will be announced in the October 1952 issue of the JOURNAL.

Financial support for these prizes is obtained from royalties received from the sale of the "Corrosion Handbook," a valuable technical volume sponsored by the Society and published by John Wiley & Sons, Inc., in 1948.

Additional information concerning the awards may be obtained by writing to the Secretary of The Electrochemical Society, 235 West 102nd Street, New York 25, New York.

Graham, Crowley Enlarges Facilities

The Research and Development Laboratories of Graham, Crowley & Associates, Inc., Chicago, have recently undergone a second enlargement within a year in order to improve and extend the electrochemical research facilities of the company.

The Chicago Division is largely devoted to research in the field of primary batteries, secondary batteries, the electrolytic recovery of rare metals, and electro-organic processes. It is under the supervision of Dr. C. A. Crowley, Research Director, and Dr. W. M. Langdon, Associate Director of Research.

The Jenkintown, Pennsylvania, Division of the company, which is engaged in electroplating, metal finishing, and electrometallurgy, will undergo a staff enlargement at an early date.

Recent additions to the Chicago staff include: Abraham Krieg, Masanobu C. Miyaji, F. D. Ortscheid, Samuel N. Block, and Thomas N. Hall.

O.W.S.

Westinghouse Talent Search—and Fellowships

The eleventh annual Westinghouse Science Talent Search began on December 10th as 15,000 science-minded, high school seniors took a three-hour science aptitude test. Of this number, 40 will be chosen to compete in the Search finals in Washington, D. C., on February 28th, and 260 more will be chosen for honorable mention.

The candidate adjudged the most promising young scientist in the nation will be awarded a four-year $2,800 Westinghouse Grand Science Scholarship. Runners-up will receive scholarships ranging from $100 to $2,000; the 260 honorable mentions will be recommended for scholarships to colleges and universities.

The Search, open to all seniors in secondary schools in the U. S., is conducted by Science Clubs of America through Science Service; it is sponsored

by the Westinghouse Educational Foundation, which is maintained by Westinghouse Electric Corporation.

* * *

From 20 to 40 fellowships—each valued at $250—will be awarded to secondary school science teachers who will participate in a special six-week summer program at Carnegie Institute of Technology. The 1952 fellowships also have been made available by the Westinghouse Educational Foundation.

The program extends from June 30th to August 8th. A $50 tuition fee will be charged for the course and the balance of the $250 can be applied to living expenses. Application forms and further information may be obtained from the Director of Admissions, Carnegie Institute of Technology, Pittsburgh 13, Pa.

New Aluminum Coloring and Derusting Processes

Two new processes of unusual interest have recently been developed by Enthone, Inc., New Haven, Connecticut.

One of these is a chemical process that in one operation provides for the protection and coloring of aluminum in such colors as yellow, blue, green, gold, brass, and other shades.

The procedure developed for coloring consists of cleaning the aluminum part and immersing it in a solution of Alumox 44 salts. Dyes can be added to the processing solution so that coating and dyeing occur simultaneously. Coloring is accomplished in from 15 seconds to 2 minutes.

Objects that have been successfully colored by the new process include aluminum hardware, jewelry, slide fasteners, buttons, automobile trim, goblets, picture frames, electrical fittings, lamps, etc.

The second development, recently announced, is a new alkaline derusting process for steel, cast iron, malleable iron, and other iron alloys. It is said to be unique in that no acid is required in the procedure, with the attendant advantages of elimination of subsequent rusting, no attack on base metal, and speed of operation. High carbon steels can be rapidly derusted without any trace of tarnish or attack. Because of its alkaline nature, the process cleans and derusts at the same time in a matter of a few seconds to several minutes. The operation of the bath is simple and derusting can be accomplished on board ship, near battlefields, or in oil well districts.

The simplicity and speed of the process are expected to make it valuable in saving large amounts of military material and industrial equipment.

Dr. Walter R. Meyer, president of Enthone, Inc., is the inventor of the two processes.

SECTION NEWS

Pacific Northwest Section

The Northwest Section held the first meeting of this season on November 26, 1951, at Bagly Hall, University of Washington, Seattle, Wash. This was a joint meeting with the Puget Sound Section of the American Chemical Society, arranged to hear Dr. K. S. Spiegler of Harvard University speak on the subject "The Electrochemistry of Ion Exchange Resins." Dr. Spiegler discussed electrochemical phenomena associated with anion and cation exchange resins, and their similarities and differences to the usual electrolytes.

The Electrochemical Society members met for dinner before the talk and again afterward to hold a short business meeting. The discussion at this time included the problem of conducting meetings of a local section encompassing a large geographical area. In addition, the following officers were re-elected for the year 1952:

Chairman—G. L. Putnam
Vice-Chairman—Glenn Ware
Secretary-Treasurer—Joseph B. Heitman

Mr. Errol H. Karr was appointed chairman of the membership committee.

Mr. F. F. Bradford of the Industrial Electroplating Works of Seattle will speak at the next meeting of the Section, to be held in February, on the subject of "Industrial Electroplating." Exact date and place to be announced.

JOSEPH B. HEITMAN, *Secretary-Treasurer*

Pittsburgh Section

The Pittsburgh Section held a meeting on November 28th at the Mellon Institute. Mr. J. M. Guthrie, Chairman of the local section, outlined briefly the program for the year 1951–52 and then introduced the guest speaker for the evening, Dr. J. V. Petrocelli, Director of Research, Patent Button Company, Waterbury, Connecticut, who spoke on the subject "Mixed Potentials and the Polarization Characteristics of Aluminum in Redox Systems."

Dr. Petrocelli gave a description of studies made of the reactivity of pure aluminum with cerium^{+4} sulfate in sulfuric acid, and also with iron sulfate in solutions of varying acid strengths. Electrode potentials, weight loss data, and polarization curves were presented, and it was shown that the reaction may be interpreted from an electrochemical point of view. The theory of the "Mixed Potential" was suggested as a more generalized concept than the local cell idea for the interpretation of the dissolution process. He gave a brief outline of the probable mechanism for the dissolution and passive behavior of aluminum.

Dr. Petrocelli further discussed his studies of the polarization characteristics of the oxidation-reduction systems, iron sulfate, iron chloride, potassium ferrocyanide-ferricyanide, and cerium sulfate. He pointed out that the experimental data strongly indicated that the overvoltage included an activation overvoltage in addition to that due to concentration polarization. He discussed the data briefly from the point of view of rate processes.

The discussion that followed the lecture gave ample evidence of the interest of the members of the Pittsburgh Section in the outstanding work described by Dr. Petrocelli. During these discussions, Dr. Petrocelli pointed out many new experimental possibilities of studying the mechanisms of electrode reactions.

R. D. WILLIAMS, *Secretary-Treasurer*

San Francisco Section

The first technical meeting of the 1951–52 season was held at the St. Julien Restaurant, San Francisco, on December 6, 1951. The guest speaker of the evening was Mr. C. E. Harvey, Director of American Spectrographic Laboratories, San Francisco. His subject was "Recent Developments in Instruments and Methods of Spectrographic Analysis."

Mr. Harvey began his talk with a discussion of the history of the development of the spectrograph, mentioning that, from the 1820's until the early 1900's, the instrument was very limited both in design and application. Since about 1930 the spectrographic field has expanded tremendously both in equipment design and in techniques. Using the instrument for quantitative analysis has been a recent trend of considerable importance.

The analysis of samples for metal content was the first field in which the spectrograph was widely used. Later the detection of nonmetals and trace elements became quite common.

The four essential parts of a spectro-

graphic analysis installation are the source unit or excitor, the dispersion unit or spectrograph, the recording medium, and measuring device. The recording medium is usually photographic film and the measuring device most commonly used is the densitometer. A new development known as the quantometer combines the recording and measuring units and is direct-reading. It promises a higher accuracy, within 0.5 per cent, compared to within 2 per cent using photographic film and a densitometer. The limit of detection with a spectrograph is about 0.001 per cent on a 10 mg sample.

The development of better spectrographic instruments has about reached a peak and the trend at present seems to be toward newer and wider applications. New techniques have also been developed that eliminate most sampling errors, being especially helpful in the field of analysis of nonmetallic materials. Mr. Harvey stated that the future of the field does not depend so much on the development of analytical equipment and techniques as it does on learning how to interpret and correlate the analytical results that are obtained.

A good portion of the meeting time was spent in a question and answer period in which there was a wide participation of the members and guests.

A business meeting of the Section was held on October 3, 1951, during which committees were appointed, programs and speakers discussed, and various other items of business taken care of.

R. F. Bechtold, *Secretary-Treasurer*

PERSONALS

C. P. Hackett, formerly chief engineer at The Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y., has been advanced to the newly created technical post of Assistant Director of Development for the company.

Bernard A. Gruber has left Battelle Memorial Institute, Columbus, Ohio, to join the staff of Metal Hydrides Inc., Beverly, Mass.

Ellis H. Gates has resigned his position as Director of Research with Cerro de Pasco Corporation, La Oroya, Peru, and will return to the United States for permanent residence.

B. K. R. Prasad, Electric Grid Offices, Government of Bombay, Bombay, India, has been appointed as a member of the committee to formulate the course of studies in Electrochemical Technology at the Andhra University, Waltair.

K. Rajagopal, Mettur Chemical and Industrial Corporation, Mettur Dam, has been made Engineering Superintendent of that corporation.

Ernest H. Wyche of Lukens Steel Company, Coatsville, Pa., is now affiliated with Colgate-Palmolive-Peet Company, Jersey City, N. J.

H. Harold Bulkowski, Houdry Process Corporation, has been transferred from Marcus Hook, Pa., to the company's plant at Springfield, Pa.

Howard A. Acheson, president of Acheson Colloids Corporation, became a member of the company's 25-year club at its annual meeting in Port Huron, Mich. Also as managing director of Acheson Colloids Limited, the English subsidiary, Mr. Acheson was inducted into their newly organized 25-year club on his recent trip to England.

JOHN B. EKELEY

Dr. John B. Ekeley, renowned scientist and retired chemistry professor, died in Boulder, Colorado, on November 8th. He was 81 years old.

Dr. Ekeley was a resident of Boulder since 1902, when he came to the University of Colorado and served as professor and head of the chemistry department for 35 years. In addition to his scientific achievements he was well known for his many community activities.

Born in Sweden in 1869, Dr. Ekeley came to America with his parents at an early age. He received the A.B. and M.A. degrees from Colgate University, and the Ph.D. degree from the University of Freiburg in Germany.

He had been a member of The Electrochemical Society since 1913.

NEW MEMBERS

In December 1951 the following were elected to membership in The Electrochemical Society:

Active Members

James G. Angevine, Ryder Scott Co., mailing add: 20 Melvin Ave., Bradford, Pa. (Corrosion and Electronics)

Jean P. Brenet, Piles Wonder, mailing add: 66 Rue Ponthieu, Paris 8e France (Battery, Corrosion, Electronics, and Theoretical Electrochemistry)

Eugene O. Brimm, Linde Air Products Co., E. Park Drive & Woodward, Tonawanda, N. Y. (Electrothermic)

Von C. Campbell, General Electric Co., mailing add: 122 Hickok Ave., Syracuse 6, N. Y. (Electronics)

Adrian H. Daane, 250 Research Building, Institute for Atomic Research, Iowa State College, Ames, Iowa (Electrothermic)

William J. Ehlen, Electro-Lab Processes, Inc., mailing add: P.O. Box 634, Cincinnati, Ohio (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

Arnold I. Friedman, General Electric Co., mailing add: 2980 E. 132nd St., Cleveland 20, Ohio (Formerly an associate member) (Electronics)

Melvin L. Friedman, National Video Corp., mailing add: 5863 N. Glenwood Ave., Chicago, Ill. (Electronics)

C. L. Fuelling, Harshaw Chemical Co., Swanson & Jackson Sts., Philadelphia 48, Pa. (Electrodeposition)

William W. Hunlock, Trilex Corp., Wayne, Michigan (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

Basil G. Hunt, The Consolidated Mining & Smelting Co. of Canada, Ltd., Trail, B.C., Canada (Electrothermic)

John A. Keralla, Electric Storage Battery Co., mailing add: 6463 Ditman St., Philadelphia 36, Pa. (Battery)

Yurii E. Lebedeff, Central Research Dept., American Smelting & Refining Co., Barber, N. J. (Industrial Electrolytic)

Russell A. Lindberg, Naval Research Laboratory, mailing add: 5320 8th St., N. W., Apt. 105, Washington 11, D. C. (Corrosion, Electrodeposition, and Electrothermic)

Joseph A. Neubauer, Columbia-Southern Chemical Corporation, mailing add: 4819 Old Boston Rd., Pittsburgh 27, Pa. (Industrial Electrolytic)

Arvin W. Rathfelder, National Video Corp., mailing add: 309 S. Grant St., Westmont, Ill. (Electronics)

Henry A. Saller, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio (Electronics)

William J. Schreiner, The Cincinnati Gas and Electric Company, P.O. Box 960, Cincinnati 1, Ohio (Corrosion)

JOHN A. SHAW, International Graphite & Electrode Corp., mailing add: 9106 Grifton Ave., Niagara Falls, N. Y. (Electrothermic)

WILLIAM STERICKER, Philadelphia Quartz Co., Public Ledger Bldg., Philadelphia 6, Pa. (Corrosion and Electronics)

JOHN A. STEVENS, Dow Chemical Company, mailing add: 1013 Rodd St., Midland, Mich. (Battery, Corrosion, and Theoretical Electrochemistry)

JUNIOR W. WHITNEY, National Lead Co., mailing add: 252 First Ave., Raritan Township, Fords, N. J. (Corrosion and Industrial Electrolytic)

Associate Members

KLAUS K. BERJU, Electric Storage Battery Co., mailing add: 1000 Rosalie St., Philadelphia 24, Pa. (Battery)

JOHN W. STETZ, Sylvania Electric Products, Inc., Ottawa, Ohio (Electronics and Theoretical Electrochemistry)

Student Associate Member

LEE J. DROEGE, University of Cincinnati, mailing add: 1404 Old State Rd., Park Hills, Covington, Kentucky (Electrodeposition)

BOOK REVIEWS

TEXTBOOK OF ELECTROCHEMISTRY, Volume I, by G. Kortüm and J. O'M. Bockris. Published by Elsevier Press, Inc., Houston, Texas, 1951. xvi plus 351 pages, $7.00.

This Textbook, based on, but much more than, a translation of Kortüm's "Lehrbuch der Elektrochemie," covers the physical chemistry of electrolytic solutions at about first year graduate level. Each topic is presented in elementary fashion and developed to the point where the student should be able to read current literature with appreciation. Emphasis is on basic principles; there is much authentic information on topics of modern interest, but no attempt has been made at completeness for reference purposes.

Chapter I deals with definitions, laws, ion migration; it contains a useful section on electric fields and energy. Chapter II introduces chemical thermodynamics, with brief and classical presentation of basic concepts, i.e., "Thermodynamics ...concerns the relation between heat and work." Nomenclature and conventions are European here and elsewhere in the book. The necessary equations are developed clearly and logically; the concept of chemical potential is introduced and used consistently throughout later chapters. Equilibria and colligative properties are treated briefly in this chapter.

Chapters III–V treat interparticle forces, solvation, ionization, and interionic attraction theory. Chapters VI–IX cover conductance and electromotive force, with theoretical and practical applications; also, weak electrolytes and acid-base theory.

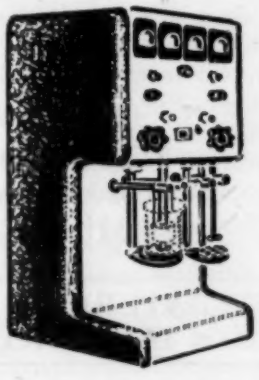
This volume has many errors of typography and proofreading, and a few sections show evidence of hasty writing. Confusing errors are found in the value of K for acetic acid (p. 146), the treatment of K_S (pp. 160–1), equation 1a (p. 228), equation 13b (p. 282), the use of a^* (p. 236), and the name mercurous oxide for HgO (pp. 293–4). On page 161, TlCl is probably a poor example (too soluble, incomplete ionization). Clearly, Sørensen did not define pH as suggested on page 283. The presence of free protons in solution (pp. 340–1) is questionable, as is the ion $Ba(SO_4)_2^{=}$ (p. 39). Use of p-nitraniline as a standard for the Hammett acidity function (p. 342) was soon outmoded.

Volume II (of about 500 pages) is to cover interfacial phenomena, irreversible electrode processes, gases, experimental methods, and is to contain tables of physicochemical data, and a section on problems. Its appearance is awaited with interest.

CECIL V. KING

GALVANIZING (HOT-DIP), third edition, by Heinz Bablik. Published by John Wiley & Sons, Inc., New York, 1950. 502 pages, $10.00.

Heinz Bablik, lecturer in the Technical University of Vienna and manager of his own galvanizing works, is in an exceptionally advantageous position to evaluate both the scientific and industrial aspects of the galvanizing process. This third English edition of his 1923 publication, "Das Verzinken von Eisen," is designed to keep his readers up to date on both these aspects. Acting on the premise that "theory is the best guide to practice," Bablik presents a detailed, well-balanced treatment of the theories of the various steps of the galvanizing process combined with current industrial methods for applying them.



Eberbach

electro-analysis apparatus

New Methods Manual prepared at Battelle Memorial Institute under Eberbach sponsorship is supplied with each apparatus. This rugged unit is built for continuous duty. Built-in rectifier delivers 8 volts, 5 amperes DC to both spindles simultaneously or 10 amperes DC for a single determination. Ammeter, voltmeter, polarity reversing switch and power control knob are provided for each position. Case is stainless steel and cast aluminum. Operates from 115 volt or 230 volt, 60 cycle AC. Unit measures 14½″ by 16½″ by 29½″ high. Ask for illustrated bulletin 130.

Eberbach CORPORATION
SCIENTIFIC INSTRUMENTS & APPARATUS
ANN ARBOR, MICH.

The book opens with a discussion of scale formation on steel during rolling and annealing. The theory of scale removal, or pickling, is then considered, followed by industrial pickling practices. A short chapter on the chemistry of fluxes precedes "Galvanizing Theory"—the predominant section of the book. The final chapter deals with galvanizing practices and procedures for examining coated products.

Completely reorganized and rewritten, the book is more limited in scope than the preceding edition, but much more detailed in treatment. Galvanizing methods other than hot-dip have been excluded. The material, notwithstanding the added detail, is presented in a more readable form. An overall impression is that this edition has been anglicized structurally as well as linguistically. Charts and illustrations are largely new and their reproduction has been improved. The Table of Contents consists of a complete listing of paragraph headings together with their locations, facilitating reference to general subjects. However, when reference to specific topics is attempted it is not an adequate substitute for the index which was omitted. Some arbitrariness has been exercised regarding literature references. Past work occasionally is specified only by the name of the worker. The periodical information presented appears parenthetically in the text, tending to disrupt continuity of thought. No bibliography is included.

These criticisms apply to the utility of the book as a reference source and do not affect its chief attribute: complete and up-to-date coverage of the subject in detail by an authoritative writer. A valuable reference to all who are concerned with this type of metallic protection, it will be of special interest to those who like to see the theoretical picture integrated with the practical.

W. W. Bradley

Mathematical Engineering Analysis by Rufus Oldenburger. Published by the Macmillan Company, New York, 1950. xiv plus 426 pages, $6.00.

This book is intended to serve as a text in courses on engineering analysis and industrial physics and as a reference work for applied scientists. It is divided into five parts entitled: I. Mechanics of Rigid Bodies, II. Electricity and Magnetism, III. Heat, IV. Elasticity, V. Fluid Mechanics. Many applications of mathematical analysis to practical problems are given in the text, which is supplemented by numerous problems at the end of each section. In most cases the emphasis is on the formulation of a physical situation in mathematical terms rather than the solution of problems. Only a knowledge of elementary calculus, vector analysis, and Green's and Stokes' theorems is required as a background. J. A. Lewis

Philadelphia Historical Exhibit

As a feature of the Fiftieth Anniversary Meeting in Philadelphia, May 4–8, 1952, it is planned to have an exhibit of apparatus and industrial equipment used in the earlier days of electrochemistry. The committee in charge of arranging this exhibit invites the cooperation of members of the Society in providing exhibit material for use during the Philadelphia meeting. Kindly address inquiries to the chairman of the committee: Arthur Osol, Philadelphia College of Pharmacy and Science, 43rd St. & Kingsessing Ave., Philadelphia 4, Pa.

MEETINGS OF OTHER ORGANIZATIONS

American Society for Testing Materials, spring meeting and committee week, Hotel Statler, Cleveland, Ohio, March 3–7.

Chicago International Trade Fair, Navy Pier, Chicago, March 22–April 6.

American Society of Mechanical Engineers, spring meeting, Seattle, Wash., March 24–26.

LITERATURE FROM INDUSTRY

*p*H Indicator Chart. A new *p*H Indicator Chart has been issued showing the hydrogen ion concentration ranges and color changes of Eastman Indicators; it also gives directions for preparation of the solution. Eastman Kodak Company. P-11

Sorbit. A new bulletin on Sorbit has been released describing the specifications, solubilization, and applications of this product. Tables included. Alrose Chemical Co. P-12

Electroplating Processes. Condensed description of special electroplating processes for cadmium, zinc, copper, nickel, and silver; technical manuals, illustrating and describing various processes in detailed form. Hanson-Van Winkle-Munning Company. P-13

Glass Equipment. 16-page booklet illustrates and describes new glass apparatus for the laboratory. Scientific Glass Apparatus Co. Inc. P-14

Heat Exchangers. Well-illustrated bulletin on heat exchangers has been issued, containing a series of charts and nomographs which greatly simplify the calculation of heat transfer requirements. Corning Glass Works. P-15

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

EMPLOYMENT SITUATION

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Physical and Electrochemist, Ph.D., 15 years' research and industrial experience in electrodeposition of metals and metal finishing, excellent educational background, thorough knowledge of all electroplating and electroforming processes, desires suitable position. *Reply to Box 347.*

Editorial

The Society and Electrothermics

"***TO PROMOTE*** **the attainment and dissemination of knowledge pertaining to high temperature processes involving heat derived from electrical energy"** has been and is the objective of the **Electrothermic Division.** This simple statement is far-reaching in scope because it implies that the electrothermic field covers not only phenomena, materials, equipment, and measurements, which make high-temperature processes possible, but also the products from these processes. These products form the basis for many of our most important industries. Also, new materials, derived from electrothermic processes, are being rapidly developed to meet the needs of new-born technologies such as jet engine propulsion and atomic energy.

The electrothermic field has been of major interest to The Electrochemical Society since its founding fifty years ago. Not only were a large number of the 350 charter members engaged in electrothermic endeavor, but the high proportion of papers on electrothermic subjects contained in the TRANSACTIONS down through the years is indicative of the importance of this field in the growth of our Society.

As the Society celebrates its fiftieth anniversary this year, the Electrothermic Division is celebrating its thirtieth as a formalized unit. During the first twenty years of the Society's history, specialized interests were assigned to "Technical Committees." By 1921 there were twenty-eight such committees and it had become evident that some consolidation was desirable. In that year the present organization by Divisions was inaugurated and the Electrothermic Division was among the first created in 1922.

When the Division was formed it absorbed individual Technical Committees

(*Continued on next page*)

on "Electric Furnaces," "Carbon Electrodes," "Carbides, Abrasives, and Refractories," "Ferro Alloys," "Electrometallurgy," "Iron and Steel," "Copper Smelting," "Zinc," and parts of several others. These fields form the backbone of early activities of the Division and many of them are described in a special feature of this issue, "Fifty Years of Progress in Electrothermics." In this special feature, articles have been written by prominent specialists, including one of the nine living charter members of the Society.

The Electrothermic Division is flexible, seeking new scientific and technological areas which are not adequately covered, and at the same time avoiding unnecessary duplication of effort in fields that are satisfactorily covered by other groups. For example, because the field of electric furnace iron and steel is now well covered by AISI and AIME, the Electrothermic Division does not attempt to be very active in this field. On the other hand, the widespread interest in the new high temperature materials, and the tremendous potential for the production and use of these materials, has caused the Division to concentrate much of its recent efforts in this area.

The Electrothermic Division has had a distinguished past, for it has brought before the Society some of the outstanding scientific and technical papers of each generation since its founding. It is alive to the important trends of the present, and it will continue in the future to act as the clearing house for electrothermic progress, which is having such a profound influence on our whole civilization.

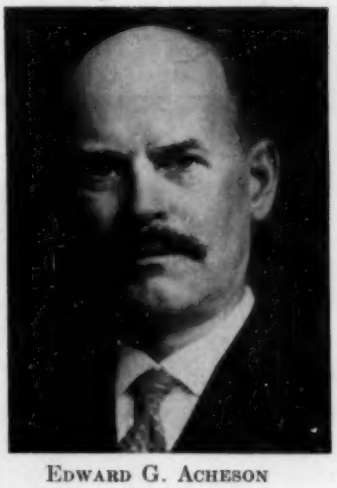
—C. H. CHAPPELL

Fiftieth Anniversary

FIFTY YEARS OF PROGRESS IN ELECTROTHERMICS

Electric Furnace Silicon Carbide Production

*G. M. Butler**



EDWARD G. ACHESON

Silicon carbide, a senior member of the family of chemicals produced by electrothermic processes, has been produced for over sixty years by a furnacing technique which is still unique in that family. This process is suitable only for the few compounds such as silicon carbide which form at high temperatures in the vapor phase without passing through a liquid condition. Except that they are larger, the modern silicon carbide furnaces differ only in relatively minor details from the first furnaces put together by Edward G. Acheson for the commercial production of silicon carbide. A patent granted to Acheson as early as 1893 describes the essentials of the present furnaces.

In going from his iron plumber's bowl and vertical electrodes to a horizontal resistor furnace, and from clay to silica and carbon, Acheson himself made the greatest change in the process. It is a testimonial to his genius that all the work done since his day has not succeeded in changing the basic details of the operation. Although it is one of the simplest of modern electrical furnaces, the horizontal, trough-type furnace, with resistor buried in the material to be converted, is still the most efficient tool for producing this man-made abrasive and refractory material.

Fig. 1 and 2 show the early furnaces used when The Carborundum Company was first organized. As the demand for the product increased, the furnace width and length was increased, as, of course, was the power input rate.

Modern silicon carbide furnaces may be up to 60 feet long by 10 or more feet wide and contain 60 to 80 tons of charge. They are batch furnaces, which must be loaded, fired for about a day and a half, and then cooled to permit unloading. At power input rates ranging up to 3000 kw, these furnaces are no longer large in comparison with many other electrothermic operations, but the industry still consumes lots of power, almost all of it hydroelectric. Each pound of silicon carbide requires from 3 to 5 kwhr, and the annual production statistics shown in Fig. 3 reveal that nearly 70,000 tons have been made in one year in the United States and Canada.

Furnace Design and Operation

Fig. 4, 5, 6, and 7 show views of a typical furnace as loaded; partly fired; with the ingot exposed ready for unloading; and during unloading of the ingot.

* Manager, Research and Development, The Carborundum Company, Niagara Falls, New York.

The original furnaces were made of brick built up on a flat base. To reduce the labor of dismantling to remove the product, the sides were changed to a single layer of brick supported on a cast iron frame curved to follow roughly the shape of the ingot.

The removable brick-lined racks forming the trough have been replaced in some companies by massive cast concrete parts, sometimes with the return leads through holes in the castings. The furnace heads, through which the electrodes extend, are sometimes made of reinforced concrete in one piece, except that the center portion is filled with a special refractory composition surrounding the electrodes. The number of electrodes in each head may vary from three or four small ones down to one large one. The resistance core through the center of the charge may consist of loose graphite laid in a trough and tamped lightly in place, or it may consist of a small solid graphite rod running the length of the furnace and surrounded either by graphite or by the so-called firesand from the outer layers of the converted material.

Practice for mixing the ingredients of the charge has been progressively improved, until now many plants have fully automatic weighing and mixing systems that almost eliminate human error and insure reproducibility.

Techniques for loading and unloading also differ in various plants. Commonly the charge is delivered in hoppers carried by overhead cranes which discharge the mix in batches down into the furnace trough. The mix may, however, be delivered in belts which traverse the length of the furnace. Various mechanical aids for unloading have been devised, although they all suffer from the hot nature of the product when the furnaces are unloaded before cooling sufficiently. The ingot is often broken up with a sort of skull crusher, into large lumps which can be removed with tongs. The graphite core must then be removed, usually by shoveling, to expose the lower half of the ingot. When this is removed, the material left in the bottom of the trough may either be removed for reworking or may be left in place and reused repeatedly as a base for the charge.

In any silicon carbide plant, transformers are the key items. One transformer will serve from four to six furnaces. Only one of these is on the line at a time; the others are in the stages of being loaded, cooled, or unloaded. Thus, rather lengthy runs of interleaved copper bus-bar must extend from the transformer to the furnace units.

The industry has profited by the electrical industry's progress in design of transformers and accessory equipment. In early installations, a water rheostat was often used to regulate the current flow and to provide means for breaking the circuit. This clumsy device was superseded by tap changing transformers, equipped with from 15 to 30 or more taps ranging from perhaps 350 volts down to about 160 volts, often with motorized devices for changing taps under load. They are commonly single phase, with three transformers constituting

a complete installation to permit operation on three-phase power.

Efforts at Improvement

Even though so little basic difference is evident between Dr. Acheson's and modern silicon carbide furnaces, much effort has gone into study of modifications and new types of furnace, along many lines.

One fertile field is that of carbon monoxide recovery. Every visitor to a silicon carbide furnace room is immediately

FIG. 1. One of the first Acheson furnaces for producing silicon carbide.

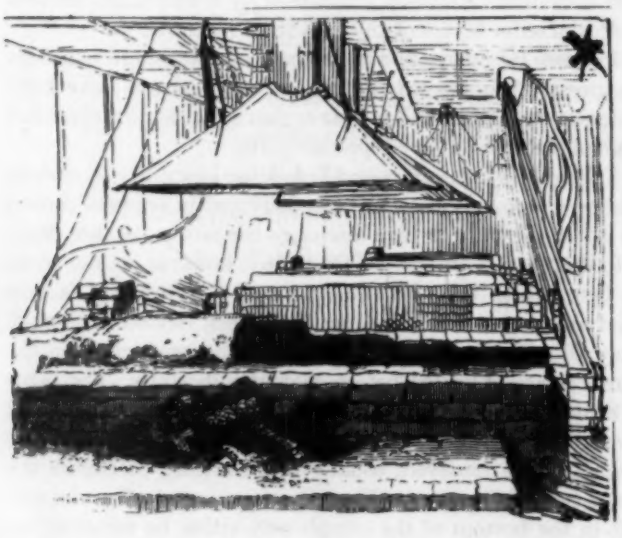


FIG. 2. Electric silicon carbide furnaces (*Scientific American*, 1894).

struck by the large quantity of gas burning above the furnace. When he is told that 1.4 pounds of carbon monoxide are produced for every pound of silicon carbide formed, he immediately asks why this gas is not recovered. Schemes for such recovery have been numerous. Some have resulted only in disastrous explosions, but in at least one case a portion of the carbon monoxide has been successfully collected and used for purposes such as generating steam or heating water. The complications of furnace operation and construction, together with their intermittent cycles and the relatively low economic value of carbon monoxide as a fuel, have discouraged many experimenters. Only if it could be accumulated in a relatively concentrated and pure form for use as a chemical reagent would carbon monoxide collection be really attractive. This would require furnaces radically different from those now employed.

Because so many other furnacing operations can be made continuous or semicontinuous, means have been sought to produce silicon carbide in continuous fashion. Early patent literature is full of ingenious but impractical schemes for this purpose. For the extremely high temperatures needed, carbon appears to be the only practical refractory. Every experimenter has rediscovered the unpleasant tendency of silicon carbide to grow wherever it can find carbon. Instead of flowing nicely through a vertical or horizontal furnace, therefore,

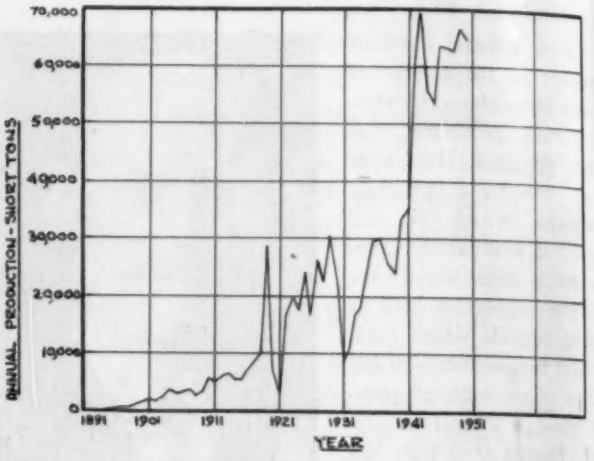


FIG. 3. Production of silicon carbide in United States and Canada by years (*Minerals Yearbook*, U. S. Bureau of Mines).

FIG. 4. Loaded silicon carbide furnaces before firing

the silicon carbide, though it can be readily formed, soon grows on all parts of the furnace until it blocks it solid. While it seems highly probable that the difficulty standing in the way of continuous production of coarse abrasive type crystals can be solved by ingenious furnace design, such a development has not yet been announced by any manufacturer. Unless it utilizes a resistor surrounded by mix, any such method is apt to suffer from lower yield per kilowatt-hour, even if it reduces the labor cost.

To save the power required to preheat the mix to temperatures attainable by fuel firing, furnaces have been designed in which a second chamber surrounds the furnace proper. Heat from fuel burned in this outer zone was supposed to penetrate the charge and bring it up to an intermediate temperature. No commercial use is known.

Events within the Furnace

Ever since Acheson's first work, experimenters have been trying to learn what happens within the silicon carbide fur-

ace. Some have tried to work on the commercial furnaces, ith probes, thermocouples, spectroscopes, and gas samplers, hile others have endeavored to set up laboratory devices to udy the process more conveniently.

These efforts have not, however, led to general agreement. his is not surprising, considering the conditions involved, t leads to doubt about several important details.

The sequence of events during heating of a furnace charge s been studied in laboratory furnaces and under the high mperature microscope‡ and appears to be about as follows:

1. Fusion of silica in the charge.
2. Reduction of silica by carbon to form molten and porized silicon metal and carbon monoxide.
3. Reaction between silicon and carbon, or perhaps carbon onoxide, to form silicon carbide of the finely crystalline bic or beta type. If carbon monoxide is the source of car- n, it is difficult to explain the mode of combination of oxy- n in the product.

FIG. 5. Silicon carbide furnace near end of firing period

4. On continued heating, the cubic crystals progressively ppear and the well-known hexagonal or alpha crystals of mmerce appear, probably through a gas phase reaction in- lving sublimation or dissociation and reforming.
5. The hexagonal crystals grow in streams of moving vapor hich carries silicon and carbon to their surfaces. Opinions ffer as to whether the vapor may contain silicon carbide as ch, in addition to silicon vapor and carbon monoxide.
6. At still higher temperatures, silicon carbide decomposes o silicon vapor and carbon, left behind as pseudomorphic skeletal graphite retaining the form and appearance of the iginal silicon carbide.

Some of the impurities in the charge, especially aluminum d alkalies, distill outwardly and condense in the cooler nes. Iron appears to stay in place unless a chloride-former present to permit formation and distillation of iron chloride. The overall reaction is quite strongly endothermic, although ne of the stages outlined may actually be slightly exother- c. The exact values are still in disagreement.

Effect of Operating Variables

Changes in charge and operating conditions can markedly er the nature of the product. The purest silicon carbide is oduced only with very pure carbon and silica, usually with addition of a material such as sodium chloride to help in latilizing some of the impurities. The crust and unreacted x from such runs cannot be reused if high purity product required, since an appreciable condensation of impurities occurred in them.

‡ Developed in The Carborundum Company Laboratories.

Materials of lower purity result in a product which is either dark green or black. Small quantities of iron alone are believed to result in green colors. Black crystals are always formed when alumina in any significant quantity is present, although the color itself may be due to finely dispersed carbon within the crystals. Since less than 0.2 per cent alumina can be dissolved in the crystal, the bulk of the alumina present, together with lime and magnesia, distill outwardly and condense in the firesand, crust, and unreacted mix.

FIG. 6. Silicon carbide ingot after removal of unreacted mix and crust.

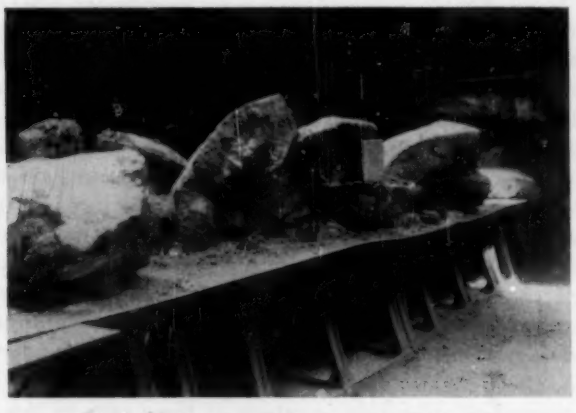


FIG. 7. Chunks of crude silicon carbide being removed from furnace, with standard brick for size comparison.

Usually the charge contains slightly more than the stoichiometric amount of carbon. When the carbon content is low, the product is apt to contain "white stuff," which may appear as masses of soft, finely cellular fibers. It may also contain free silicon. By overheating a silica-rich charge, dense silicon carbide is produced, quite unlike the usual loosely-joined crystalline masses.

Variations in furnacing must also control the type of hexagonal crystals which form. Over thirteen polymorphic but closely related types have been fully described, although one type predominates. Of considerable theoretical interest would be an exposition of the factors which influence the type of crystal in the charge.

Uses

The past fifty years have seen a greater change in the uses of silicon carbide than in its manufacture. Dr. Acheson first sold it as powder for gem cutting, and this was a major use for quite a period. Grinding wheels were made of it as early as 1892, and abrasive paper and cloth coated with it was being used in 1897. Use as a metallurgical reducing agent is re-

ported prior to 1900, and refractories and nonslip products made from it appeared soon after the turn of the century.

The nonabrasive uses of silicon carbide have arisen from discovery of its very interesting physical and chemical properties. Besides being very hard, second only to diamond and boron carbide, this compound displays a strange combination of chemical inertness under some conditions and ready reactivity under others, plus good electrical and thermal conductivity that make it a very interesting and versatile product.

Its unique electrical properties have led to development of resistors and rectifying crystals for radio sets and to nonmetallic heating elements which extend electric heating to temperatures unobtainable with metallic resistors. Its property of emitting light under passage of small currents led to efforts, quite unsuccessful, to make lamps from it. Its high efficiency of infrared radiation has resulted in therapeutic and heating applications. Lightning arrestors for power lines to pass high voltage surges, but break the current flow at normal voltages, represent a use of its special electrical characteristics.

Its high temperature strength, high thermal conductivity, and stability have made it a valuable super-refractory material for many uses, including kiln furniture, muffles, and other vital parts of furnaces. Its resistance to abrasion is leading to widespread use to resist wear in industrial processes.

As a chemical, its reactivity in molten iron and slags has led to wide use as a reducing agent and deoxidizer, especially in gray iron melting. Since halogens react with it at elevated temperatures, it has been used to produce silicon tetrachloride for manufacture of silicones. In bonded form, it has found acceptance as a catalyst support.

The next half-century should see many new uses for this versatile product as better ways to bond it and to use its electrical and chemical properties are found. Between 40 and 50 per cent of its present uses are nonabrasive in nature, and it seems safe to forecast that this proportion will become even greater.

A detailed bibliography on silicon carbide is available from The Carborundum Company, Public Relations, Niagara Falls, New York.

Carbon and Graphite Electrodes

*C. G. Ollinger**

Since carbon is the most universally known and used element in the scientific world today, it follows that countless phases of everyday human activity are closely related to it, whether directly or indirectly. Exploitation of the world's natural resources has come about through the electro-sciences, which could not be practical without manufactured carbon in either the amorphous or graphitic form. Our water, our food, our clothing, recreation, medicine, transportation, personal comfort and welfare, and now atomic energy, are directly dependent upon carbon or graphite. The world progressed and prospered for many centuries before the advent of the electrochemical and electrometallurgical industries; but the myriad of present-day products of these sciences can be traced to the progress made in the development of carbon and graphite electrodes and anodes and their uses in the electrothermal and electrolytic fields.

The brilliant record of carbon and graphite manufacture and application can be assigned to three unrelated incidents in scientific discovery, the first of which occurred in 1800 when Sir Humphry Davy made an electric spark jump between two rods of charcoal. Practically coincidental with Davy's demonstration was the discovery by Cruickshank that an electric current breaks common salt into sodium and chlorine. Only minor and, for the most part, unsuccessful efforts were made to utilize this new knowledge for several years because of the limitations of the voltaic pile battery as a power source.

The third incident occurred in 1831 when Michael Faraday, a British physicist and chemist, discovered the principles of electrical induction, permitting the conversion of mechanical work into electricity. Shortly thereafter Pincinotti, Siemens, Wheatstone, Gramme, and others began the development of the dynamo.

After Davy's first use of charcoal as electrode material, it was not until 1846 that Staite and Edwards patented a process for making carbon electrodes from pulverized coke and sugar. The mixture was molded under high pressure and the shaped mass baked at a white heat. The electrodes then were dipped in a concentrated sugar solution on the assumption that the sugar would enter the pores and make the mass denser after a second baking. This was, without doubt, the first attempt to impregnate carbon to improve its commercial properties.

Lenolt went a step further in the same year. His prepared carbon consisted of 2 parts of retort coke, 2 parts of wood charcoal, and 1 part liquid tar. The materials were worked into a paste, well kneaded, molded, pressed, covered with sugar syrup, and subjected to a high temperature for 30 hours or more. Lenolt also tried, but with limited success, to purify carbons by immersion in acids before baking. The acid treatment must have had merit at the time for Watson and Slater were still experimenting with it in 1850.

However, by 1857 LaCassagne and Theirs were attempting to purify electrodes by immersion in fused caustic soda or potash in the hope that the silica in the carbon might thus change to soluble silicates. After fusing, the electrodes were steeped in hot water and exposed to a current of chlorine gas in a porcelain tube. It was supposed that the various earths not affected by the soda or potash would be converted into volatile or soluble chlorides, which would produce a purer carbon.

At about this time Cumer conceived the idea of making carbons of a mixture of lampblack, benzine, and turpentine. This mass was kneaded, pressed, and baked, to produce a porous coke, since the benzine and turpentine volatilized during the baking. Whether Cumer knew or cared, he had made the first porous carbon, then immediately attempted to increase the density again by saturating the electrodes with resins and subjecting them to a second baking.

There were others, during this same period, who were concerned with the materials for making carbon as with the methods. Gaudin began with resins, pitch, tars, and oils, and heated the mixtures in closed vessels. The volatile products

* National Carbon Company, Division of Union Carbide and Carbon Corporation, New York, N. Y.

of these substances were condensed and collected for use again in mixing. He proceeded by pulverizing the carbon left after the decomposition and mixing it with lampblack, using the condensed volatile products as binding material. The mixture was well kneaded, molded in steel molds under hydraulic pressure, and baked. The electrodes were considered superior to others in commercial use at the time.

A U. S. patent was granted to De Grasses B. Fowler in 1858 for the process of making carbon plates by mixing ground coke with tar, shaping the mixture under pressure in molds, packing the shaped material in lime and heating it slowly in an airtight box to drive off the volatile matter.

From a commercial standpoint Carre appears to have been the first to have conspicuous success in producing carbons. His carbon mixture, patented January 16, 1876, consisted of 5 parts of very pure, finely pulverized coke, 5 parts of calcined lampblack, and 7 to 8 parts of syrup of sugar. The powders were moistened either with syrups, gums, gelatine, or with fixed oils thickened with resins, to form a paste sufficiently plastic and consistent to be forced into cylindrical rods through a drawplate at the bottom of a powerful press at about 100 atmospheres. The rods were piled into retorts and baked at a high temperature, to produce the first extruded electrodes.

Certainly great tribute should be paid these early pioneers who contributed so much to research because there was little hope for commercial reward until the year 1867 brought the first practical dynamo, which was the key that unlocked the pent up potentials of the electro-scientific age.

Charles F. Brush, of Cleveland, entered the field of practical and commercial electricity in 1876 with his version of the dynamo and a carbon arc lamp in which the arc was controlled by the current. The carbons that Brush used in his first demonstrations were sawed out of gas retort carbon, but very shortly he, in collaboration with W. H. Lawrence, his plant superintendent, used raw petroleum coke by pulverizing it, mixing with a binder, and molding to shape. Difficulties with the densities led them to the invention of the process of calcining coke. Added to this important development was the invention of a hydraulic press which is practically of the same shape and construction as those used today.

The inventions of Thomas A. Edison in the field of electrical generation were milestones that were to accelerate electro-developments because of increasing efficiency, less faulty operation, and greater stability in current output. Edison's work with the incandescent lamp also added immensely to furthering the graphite industry. Edward G. Acheson, who played such a dominant role later on, entered the field as superintendent of the lamp factory at Menlo Park, and successfully produced small graphite lamp filament drops in large quantities.

The much earlier electrolytic process of Cruickshank began to take commercial form as soon as more abundant electric power became a reality. The first American patent was issued on a circular, mercury cathode cell in 1883, to A. L. Nolf, a Belgian. There were no graphite anodes in this design and the cell was never tried out; nevertheless, it does mark the beginning of the caustic-chlorine industry.

The uses of electrodes were becoming sufficiently broad and certain to warrant the organization of companies for their exclusive manufacture. The Cleveland Carbon Company was formed by two partners, Crouse and Tremaine, in 1884. Their importance to the industry is memorialized in the Crouse-Tremaine Works of National Carbon Company, Fostoria, Ohio. The Bolton Carbon Company had been formed to help satisfy the demand for lighting carbons. W. H. Lawrence, who was associated with the Brush Electric Company, bought an interest in Bolton in 1886 and by the end of that year the organization name was changed to National Carbon Company with Lawrence as its first president.

While the manufacture of arc carbons, battery plates, and electrodes was adding important knowledge to carbon chemistry and improved methods of manufacture, the development of the electric furnace gained headway as soon as the power problem was solved in 1867. Twelve years after the first dynamo was built Siemens patented both his horizontal and vertical types of electric furnaces, and in 1886, Heroult produced the first of the many types of electric furnaces to bear his name. In the same year Hall invented his process for producing aluminum, antedating Heroult slightly.

Major James Turner Morehead and Thomas L. Willson decided to use the power developed from the Dan River, in North Carolina, to make aluminum from its oxide in the intense heat of the new electric furnaces. They organized the Willson Aluminum Company and built a small plant near Morehead's practically defunct cotton mill at Spray, North Carolina. There in 1892, after many failures to get aluminum, a grayish, crystalline substance emerged from the furnace and the furnaceman attempted to quench it with water. Volumes of gas rewarded his efforts, for the gray material was calcium carbide and the gas was acetylene.

Acheson had become interested in making a much-needed abrasive. He severed his connections with Edison and began experimenting. He made a furnace from a plumber's iron solder melting pot, filled it with clay and powdered coke. Using the pot as one terminal and a lighting carbon as the other, he melted the clay and succeeded in making the first artificial abrasive material for which a druggist friend helped coin the brand-name "Carborundum." A short time later Acheson organized The Carborundum Company.

One of his first accomplishments was the development of a furnace in which materials could be processed for making the new abrasive; Acheson also was thinking in terms of artificial graphite. In 1897 he built the first graphitizing furnace in the world, to usher in the graphite phase of the manufactured carbon industry.

The opportunity to begin graphitizing operations was given to Acheson by H. Y. Castner who was designing and installing mercury cathode cells for the Mathieson Alkali Works in Niagara Falls. Castner approached Acheson to graphitize carbons which he had purchased from the Washington Carbon Company. The first load of oval anodes, ⅞ x 1¼ x 15 in. in size, was delivered to The Carborundum Company in May 1897 for graphitizing. The furnace was 16 feet long between the heads. The first charge consisted of 2905 carbons weighing 2300 pounds which were piled crosswise in order to keep the resistance of the furnace as high as possible. The carbons were stacked as solidly as possible, in view of their shape, in a single pile one foot high between the two furnace heads, and a two-inch layer of powdered coke was placed around the pile to prevent contact between the carbons and the carborundum mixture which surrounded the whole load. Power was applied on June 7, 1897, and the run continued at 7800 amperes. The end of the run was determined by guess work.

During the balance of 1897, 142,500 pounds of anodes were treated. From June 1897 until July 1900 all graphitizing for the several carbon manufacturers was done by The Carborundum Company, at ¼ cent per pound.

Acheson had secured many patents on his "purified carbon" between 1895 and 1899, and in 1900 The International Acheson Graphite Company was formed to encompass also the

British and French patents he had obtained. At this time he became disturbed by the stub loss in electrode use, because they were nonjoinable, and started the manufacture of joinable electrodes. Shortly thereafter he had improved the method to embrace the threaded socket and separate threaded nipple that is used universally today. By 1910 International Acheson was producing more than a million pounds of graphite per year.

Heroult had been active in the aluminum industry and invented equipment for improving and forming carbon electrodes. Hardmuth, an Austrian lead pencil maker, probably was the first to make large electrodes by extrusion. He also was the first to use anthracite, although he did not calcine it, in making electrodes for ferroalloy furnaces.

The aluminum industry must receive credit for pushing the development of furnace electrodes, for as the demand for aluminum increased, so too did the demand for larger and larger pots and electrodes. The aluminum electrode business had grown to such an extent that by 1904 National Carbon Company, Inc., was required to build a special plant at Clarksburg, West Virginia, to supply carbon electrodes to the aluminum companies and to Acheson Graphite Company.

With the background of aluminum production to draw upon, the electric furnace steel industry began to make its weight known around 1900, although the first electric steel was not made until 1906, at the Holcomb Steel Company, in Syracuse, New York.

The first furnace electrodes were made of carbon and were imported principally from Germany and Sweden. There were difficulties with the quality and delayed deliveries which put pressure on American companies. By 1906 National Carbon Company was delivering carbon electrodes as large as 8 in. diameter and 48 in. long, made of finely grained petroleum coke material. Beginning in 1908, electrodes were composed of electrically calcined coal, molded to shape and fired in saggers. The Electrode Company of America was formed by Hercult in Niagara Falls in 1910, with equipment to make carbon electrodes. The first hydraulically pressed furnace electrodes were made in 1913.

World War I, in 1914, propelled a rapid expansion of the electric furnace industry and the electrode manufacturers kept pace. During the war years National Carbon and Acheson Graphite worked together in producing electrodes up to 14 in. diameter. The quality at that time was greatly inferior to accepted standards today and there was trouble with breakage. The emergency was bridged, however, and the experience gained served to enhance quality control and improve manufacturing methods.

The war had made its demands on aluminum too, and there was a close affinity between aluminum and caustic-chlorine cells. A plant was built in 1916 at Niagara Falls for the production of metallic aluminum from aluminum chloride. Wheeler cells were installed for the production of chlori but aluminum production experienced indifferent succes The experience did add immeasurably to chlorine cell de velopment, and further broadened the application of carbo and graphite electrodes in the electrolytic field.

The period between the two World Wars was significan for the advancement made in the manufacture of carbon an graphite electrodes in many sizes and shapes, as well as the application in electric furnaces and electrolytic cells. Further more, it witnessed the successful adoption of other carbo and graphite products in metallurgical, chemical, processin electrical, and mechanical uses.

Just as the first World War gave a boost to the electri furnace, so World War II added tremendous impetus to th electrochemical industry. As for carbon and graphite, th electrothermal and electrochemical advances were contin ous, often paralleling and always supplementing each othe

The demand for larger and larger electrodes, which begu in the early 1900's, always has been satisfied. Carbon ele trodes were first made in the 30 in. diameter size in 1926, th 35 in. diameter followed in 1927, and the 40 in. diameter i 1930. Currently they are being made in 45 in. diameter.

The war experience of 1914–1918 in making 12 and 14 i graphite electrodes was used to advantage when the demand of the industry made it necessary to produce a 16 in. diameter The 18 in. diameter was first made in 1930, but it was n until 1937 that the 20 in. was available. Graphite electrod are at present being made in 24 in. diameter and up to 110 i long.

The general operations in the manufacture of electrod have remained practically the same for some time: calcinin grinding, mixing, shaping either by molding or extrusi baking and graphitizing. Improvements have been made each of these steps and major progress has been made regulating purity, resistivity, hardness, increased densit etc. The earlier workers tried to obtain higher densities b saturating the baked shapes with binders and baking a secon time. At present the end is reached by starting with high density materials and calcining them in a manner that w increase this factor.

The future of the manufactured carbon and graphite i dustry can be but a projection of the past trend and i present status. From its rough, practically unknown and u controlled beginnings have evolved a multitude of produc ranging from small, finely machined mechanical and ele trical parts, through porous and impervious grades, to mas moth blocks for lining metal furnaces.

With such a record of accomplishment and the fundament interrelationship of these industries, who can predict t future growth of the electrothermic industry, the yet u known channels of electrochemistry, and the eventual utili of that still shapeless monster that we know as atom energy.

Arc Furnace Practice in the Manufacture of Aluminous Abrasives and Refractories

*John A. Upper**

In 1900, C. B. Jacobs patented a process for the manufacture of aluminous abrasives by the electrothermic fusion and reduction of bauxite ore. Prior to this event, only natural aluminous abrasives such as corundum and emery were available in commercial quantities. In Jacobs' patent, the electrothermic process was carried out in a refractory lined crucible. Carbon blocks or a cementlike mixture which required baking before use were frequently used for the lining. The expense of these special linings which had to be torn down after each use, together with the care and labor necessary to build them up each time, were serious objections to the Jacobs' process.

In 1904, Aldus C. Higgins of Worcester, Massachusetts, invented a water-cooled electric furnace that turned out to be the basic tool of the aluminous abrasive industry. In his patent, Higgins disclosed an unlined rolled-steel shell, about ¼ in. thick, in the shape of the frustum of a cone, circular in cross section and tapered, being larger in diameter at the bottom. By means of a water spray at the top flange, water was cascaded down the outer periphery of the shell, forming a continuous blanket of cooling water over the entire outer surface of the shell. The furnace bottom or hearth, on which this shell rested, consisted of a metal structure in the form of a circular tray which was lined with refractory blocks, usually made of carbon.

At that time, perhaps the most startling feature of this invention was the fact that molten alumina at a temperature of approximately 2000°C could be contained in an unlined steel shell, with steel melting at about 1400°C. The reasons for this remarkable behavior, of course, were:

1. The molten alumina, of relatively high purity, was at a temperature only slightly in excess of its rather sharp melting point.

2. It was necessary to extract only a small amount of heat from the molten alumina (by means of the water-cooled steel shell) to effect solidification.

In this way, Higgins' water-cooled steel shell formed its own crucible lining of solidified fused alumina. The molten bath would approach the steel shell up to the point where the water cooling became effective, then the molten alumina would solidify forming, in situ, a solid refractory alumina lining.

In these early days, the rate of power input to the furnace was controlled in, what seems today, a rather amusing fashion. The rectangular carbon electrodes were drilled and bolted directly to the stationary bus-bars carrying power to the furnace. The entire water-cooled furnace shell and carbon-lined furnace bottom were then mounted directly on the ram of a hydraulic cylinder. When the rate of power input exceeded the desired amount, the whole furnace was lowered away from the electrodes, increasing the length of the arc, increasing the total resistance in the circuit, and thereby lowering the rate of power input. Conversely when the rate of power input was too low, the entire furnace was raised by means of the ram, bringing the bath closer to the stationary electrodes, decreasing the length of the arc, decreasing the total resistance in the circuit, and thereby increasing the rate of power input. If one electrode burned off more quickly than the other, there really was trouble. In those days, the ram was operated by the furnace operator by means of a manual valve. There were no automatic furnace power-regulating devices in use. The idea of raising and lowering the whole furnace, rather than the electrodes, was perhaps due to the fact that Aldus C. Higgins' father, Milton Prince Higgins, was a manufacturer of plunger elevators.

The changes in the Higgins' furnace over a period of fifty years have been rather few and far between. There has been a gradual evolution rather than a series of drastic changes. Perhaps the one obvious change has been making the furnace stationary and moving the electrodes to control the rate of power input. There have been some improvements in the construction of furnace bottoms. The original idea was only to have the furnace bottom refractory contain the molten alumina. Subsequently, the idea of incorporating some thermal insulation occurred, and built-up bottoms consisting of a layer of insulating material surfaced by a layer of carbon were constructed, adding somewhat to the thermal efficiency of the process.

Naturally enough, the size of the furnaces have increased with the demand for aluminous abrasives. The original furnaces had a capacity for producing about 3000 to 5000 lb of product per run. This size has gradually increased to capacities of 10,000, 20,000, and 50,000 lb, while the most popular size is still about 20,000 lb. Accompanying increased furnace size has been an increase in the rate of power input. Early furnaces had a rate of power input of about 300 kw. This rate has been increased in increments to 500 kw, 750 kw, and 1000 kw. It is understood that, at the present time, there are in operation a few commercial arc furnaces having power input at a rate of several thousand kilowatts. Coincidental with the increased rates of power input, the furnace operating voltage has increased, but to a much less marked degree.

Automatic furnace power-regulating devices have now been in use for many years. The earliest models consisted of a converted recording wattmeter, on which were mounted supplementary contacts which actuated solenoids to close switches, and drive motors connected to gear reducers, which raised and lowered electrodes by means of drums, cables, and pulley systems, to return the power input to the desired value. In these earlier wattmeter type controllers "hunting" was a very real problem. "Hunting" is due to overcorrection, i.e., raising or lowering the electrodes too far. With these primitive controllers, power input fluctuations from 0 to 200 per cent of the desired load were not at all uncommon. However, at the present time, there are many different types of controllers on the market, designed to hold the rate of power input within narrow limits of the desired set point.

The early arc furnaces were for the most part operated on single-phase power. The furnaces were small and as the demand for their products grew, production was simply increased by adding more small furnaces. With a multiplicity of small single-phase units, it was and is quite feasible to maintain a balanced three-phase load by dividing up the units per phase equally. The most modern arc furnaces of intermediate and high rate of power input now operate on three-phase power, and are equipped with three electrodes instead of two.

So far as electrodes are concerned, the early furnaces were

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operated on rectangular carbons made in one piece. When the electrode burned off to such an extent that the electrode clamp was in danger of becoming overheated and burning off, the operation was interrupted, the stub was discarded as waste, and a new electrode assembly installed. Subsequently, cylindrical carbon and graphite electrodes of greatly improved durability were made with threaded ends. By means of these threaded ends, waste was virtually eliminated, and lost time in changing electrodes was greatly reduced.

Since fused alumina abrasive is also a very good high temperature refractory, it seems quite logical that the production of fused alumina led the abrasive manufacturers into refractory and allied fields. The same Higgins' arc furnaces that produced fused alumina abrasives and refractories were used to produce other types of high-melting refractory materials.

One of the better known refractories now produced in Higgins' furnaces is electrically fused magnesium oxide. At least two grades of this material are manufactured commercially. The "Refractory" grade is used for the manufacture of bricks, crucibles, etc. The "Electrical" grade is used for the manufacture of tubular heating elements for stoves, etc. The electrical grade is a good thermal conductor and a good electrical insulator—a unique combination.

Other high-melting refractory products of the Higgins furnaces include such items as fused thoria, fused stabilized zirconia, fused lime, spinel, kyanite, sodium aluminate, fused dolomite, anhydrous boric acid, and borides and carbides of zirconia, titania, etc.

In conclusion, it may be noted that while no very radical changes appear to have been in the Higgins furnace process for the manufacture of fused aluminous abrasives and refractories, it is evident that the scale of operations has been vastly increased. A considerable increase in thermal efficiency has been achieved and a great diversity of new high-melting refractory products has been developed from the one basic tool—the Higgins arc furnace.

New Refractories—Carbides, Borides, Nitrides, Silicides

*G. R. Finlay**

This article is concerned principally with the refractory carbides, borides, and nitrides. In one respect these compounds are not new, since many of them have been known for at least 50 years. However, interest in the application of these materials in science and industry has increased greatly in recent years, and methods for preparing them in quantities ranging from pounds to tons have been developed or are in the process of development. A condensed source of information on these refractories first became available in 1897 when Henri Moissan published "Le Four Electrique" in Paris, France (1). This book summarized his researches on electric furnace products up to that date. An English translation appeared in the United States, under the title "The Electric Furnace" in 1904. Most of the presently known carbides, borides, nitrides, and some silicides were discussed in this book. As might be expected, many of Moissan's conclusions have had to be revised in the light of more recent work, but his book provided the first compendium on this subject, and is still useful to workers in this field.

In 1905, O. P. Watts (2) of the University of Wisconsin wrote a monograph covering the preparation of borides and silicides, and summarizing the information available at that time.

By 1909, Ezekiel and George Weintraub (3), working in the United States, succeeded in preparing fairly pure boron by depositing it on a hot carbon tube from a mixture of BCl_3 and H_2. They also performed one of the first hot-pressing operations by compacting boron powder to a coherent solid in a mold lined with boron nitride. The boron powder was heated by passing a current directly through it, until the temperature approached 2000°C. An auxiliary heater served to preheat the column of boron or other refractory material.

Tungsten carbide (4) first appeared in Germany in 1914, but attracted little attention until a cemented carbide became available in 1927 as "Widia" (5). This product was made by bonding fine tungsten carbide with metals of the iron group. The descendants of the original "Widia" are now familiar in industry under a variety of trade names, such as Carboloy, Kennametal, Wickaloy, Ramet, etc. The machine tool owes much of its progress to the availability of these materials for tool bits and wear-resistant surfaces. Cemented carbides have also been widely employed in such diverse fields as rock-drilling and wire-drawing.

Titanium carbide was discovered in 1887 by Shimer (6) and zirconium carbide by Moissan (7) in 1896. These compounds did not attract commercial interest until comparatively recently. Titanium carbide has become an important ingredient of the steel-cutting grades of cemented carbide tool bits. Metal-bonded (cemented) TiC is currently being promoted as a semimetallic refractory (8). Zirconium carbide is used as a raw material for the manufacture of zirconium tetrachloride, an intermediate in one process for making metallic zirconium.

A mixed carbide and nitride of titanium, apparently a solid solution of TiC and TiN, was discovered in 1850 by Wöhler (9). It has variously been known as titanium carbonitride and titanium cyano-nitride. Currently it is being used to make $TiCl_4$ for smoke screens and for the production of metallic titanium.

About 1933 a product made from coke and fused B_2O_3 in an enclosed resistance type of furnace was placed on the market (10). This material was determined to be, in the pure form, a definite chemical compound of the form B_4C. This was the first commercial production of a material harder than silicon carbide. Boron carbide is still the hardest material made by man. Under the trade name Norbide it has been used in sandblast nozzles and in many other wear-resistant applications in which its hardness is an asset. Norbide is fabricated into simple shapes by hot pressing the powdered material in graphite molds at temperatures above 2000°C.

The technique of hot pressing in a graphite mold, which was first developed for Norbide, has since been applied to the fabrication of a wide variety of carbides, borides, nitrides, silicides, and oxides (11). Patents covering furnaces and procedures have been issued to R. R. Ridgway, A. H. Ballard, B. L. Bailey, and others (12). Temperatures ranging up to 2300°C and pressures to 10,000 psi have been successfully employed. Early furnaces were heated by graphite tube re-

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sistors but of recent years high-frequency induction has also proved convenient as a source of heat.

In addition to the publications of Moissan and Watts previously mentioned, there have been a number of other contributions in this field. "Gmelin's Handbuch der Anorganischen Chemie," No. 13 published in 1926, contains a thorough compilation to that date of data on boron and borides. Karl Becker's book "Hochschmelzende Hartstoffe" (13) appeared in 1933. It provides an excellent summary of the preparation and properties of carbides, borides, nitrides, and related compounds and is still the primary source book for workers in this field.

The Atomic Energy Commission has been particularly interested in compounds of uranium and thorium. Its research workers have produced the carbides, borides, nitrides, and silicides of these two elements and have published a considerable volume of literature on their preparation and properties (14).

TABLE I. *Compounds of metals with metalloids*

Metal	Metalloid group			
	B	C	N	Si
Al	AlB_2	Al_4C_3	(AlN)	
	AlB_{12}			
Ca	CaB_6	(CaC_2)		
Ti	TiB_2	TiC	TiN	
	TiB_x(?)			
V	VB_2	VC	VN	
Cr	CrB	Cr_3C_2	Cr_2N(?)	
	CrB_2	Cr_4C_3		
		$Cr_{23}C_6$		
Zr	ZrB_2	ZrC	ZrN	
Nb	NbB_2	NbC	NbN	
Mo	Mo_2B	Mo_2C		$MoSi_2$
	MoB			
	MoB_2			
	Mo_2B_5			
Ta	TaB_2	TaC	TaN	
		Ta_2C	Ta_2N	
W	W_2B	WC		WSi_2
	WB	W_2C		
	WB_2(?)			
	W_2B_5			
U	UB_2	UC	UN	
	UB_4	UC_2		
	UB_{12}	U_2C_3		
Th	ThB_4	ThC		
	ThB_6	ThC_2		

There seems to be no up-to-date compendium of information in the general field of carbides, nitrides, and borides. The appearance of such a work would be a considerable help to workers in this field.

Tables I and II list the compounds considered in this paper. They are intended to be suggestive rather than exhaustive since a critical sifting of the literature would be a major task.

These compounds are characterized in the main by bonds of high energy as evidenced by their large heats of formation. The strong bonds also show up in two other ways:

1. The compounds are very hard, clustering about 9 on Mohs' scale or mostly above 2000 on the Knoop Hardness scale.

2. The compounds have very high melting points ranging above 2000°C or 4000°F.

A further remarkable feature of these materials is the frequency with which they show metallic properties. Most of them have a metallic luster and high thermal and electrical conductivities, which are definitely metallic characteristics (15). Exceptions to the rule are such materials as B_4C and SiC which are compounds of a metalloid with a metalloid. These substances are semiconductors. The notable exceptions are diamond and BN which are substantially insulators.

Three methods of laboratory preparation have stood the test of time and are still used for making small quantities of these compounds. These are listed below:

1. Reaction of the elements with each other, or of one element with an oxide of the other, at high temperature in a controlled atmosphere.

2. Deposition on a hot surface from a mixture of gases capable of decomposing or reacting to form the desired compound.

3. Formation by the electrolysis of a fused salt.

The first method may be illustrated by the following equation:

$$TiO_2 + 3C = TiC + 2CO \uparrow.$$

This reaction is usually carried out at 2000°–3000°C in an enclosed furnace with particular care to exclude air.

The second method, commonly known as the "hot-wire" technique, has been described in some detail by Becker. This

TABLE II. *Compounds of metalloids with metalloids*

Metalloid	Metalloid group			
	B	C	N	Si
B	Boron	B_4C	BN	—
C	B_4C	Graphite / Diamond	(C_2N_2)	SiC
N	BN	No hard compound	(N_2)	Si_3N_4(?) Si_2N(?)
Si	No compound identified	SiC		Silicon

interesting application of electrothermics was employed by the Weintraub brothers, as already mentioned, for the production of boron. In 1922, F. Koref (16) adapted the idea to the production of pure metals and was the first to use a metallic wire. In 1923, A. E. Van Arkel (17) succeeded in depositing titanium metal (iodide titanium) on a hot wire by decomposing titanium iodide, and the next year he prepared titanium carbide by a similar technique. On a laboratory scale the gaseous mixture of raw materials is passed over a heated filament of tungsten (wolfram) or tantalum wire on which the product is deposited. The following typical equation ignores possible side-reactions:

$$2TiCl_4 + N_2 + 4H_2 \rightarrow 2TiN + 8HCl.$$

The third method has been described rather completely by Andrieux and coworkers (18) who have applied fused salt electrolysis to the synthesis of borides.

Commercial methods of production have been, in general, expanded versions of the methods already described. The following examples are typical:

1. Zirconium carbide is made by reacting zirconia and carbon in an enclosed resistance-type furnace (19).

2. Elemental boron has been made by passing a gaseous mixture of boron trichloride and hydrogen over heated graphite rods (20).

3. Zirconium boride has been made in semicommercial

quantities by the electrolysis of a fused borate bath containing a small amount of zirconia (21).

For the most part, commercial use and even research have been hindered by the high cost of production of many of these compounds. The more esoteric of them will probably continue to be costly because of the small quantities involved and the highly specialized equipment required for their manufacture. This situation is gradually changing, as evidenced by the recent appearance on the market of high purity BN at a great reduction over previous prices. However, more economical production methods will come only when industrial research workers find large-scale applications for these compounds.

References

1. Henri Moissan, "Le Four Electrique," Steinheil, Paris (1897); H. Moissan, "The Electric Furnace," translated by Victor Lenher, 2nd ed., The Chemical Publishing Co., Easton, Pa., (1920).
2. Oliver P. Watts, "An Investigation of the Borides and the Silicides," *Bull. Univ. Wis. No. 145, Eng. Ser. No. 3*, 251 (1906).
3. Ezekiel Weintraub, *Ind. Eng. Chem.*, **3**, 299 (1911); **5**, 106 (1913); U. S. Pat. 997,879, July 11, 1911; 1,019,391; 1,019,393; 1,019,394; and 1,019,569, March 5, 1912.
4. Lohmann and Voigtländer, German Pat. 286,184; 289,066 (1914).
5. Franz Skaupy, *Z. Elektrochem.* **33**, 487 (1927).
6. P. W. Shimer, *Proc. Roy. Soc. (London)*, **42**, 89 (1887); *Chem. News*, **55**, 156 (1887).
7. Henri Moissan, *Compt. rend.*, **122**, 651 (1896).
8. J. C. Redmond and E. N. Smith, *J. Metals*, 1, 987 (1949).
9. F. Wöhler, *Ann.*, **73**, 34 (1850).
10. R. R. Ridgway, U. S. Pat. 1,897,214, Feb. 14, 1933; *Trans. Electrochem. Soc.*, **66**, 117 (1934).
11. R. R. Ridgway and B. L. Bailey, U. S. Pat. 2,027,786, Jan. 14, 1936; U. S. Pat. 2,091,569, Aug. 31, 1937.
12. R. R. Ridgway and B. L. Bailey, U. S. Pat. 2,121,74[illegible] (1938). R. R. Ridgway, U. S. Pat. 2,123,158 (1938); 2,125,588 (1938); 2,155,682 (1939). R. R. Ridgway and B. L. Bailey, U. S. Pat. 2,150,884 (1939). A. H. Ballard, U. S. Pat. 2,538,959 (1951); 2,567,592 (1951).
13. Karl Becker, "Hochschmelzende Hartstoffe und ihre technische Anwendung," Verlag Chemie, Berlin (1933).
14. Leo Brewer, *et al.*, A.E.C.D. 2823, (Feb. 14, 1950); M. W. Mallett, *et al.*, *J. Electrochem. Soc.*, **98**, 505 (1951); Leo Brewer, *et al.*, AECU 607 (UCRL 434) (Aug. 28, 1949).
15. G. R. Finlay, "Refractories for 4000°F and Higher," To be published in *Chemistry in Canada* (1952).
16. F. Koref, *Z. Elektrochem.*, **28**, 511 (1922).
17. A. E. Van Arkel, *Physica*, **3**, 76 (1923); **4**, 286 (1924); "Reine Metalle—Herstellung—Eigenschaften—Verwendung," Julius Springer, Berlin (1939) [litho-print by Edwards Bros., Ann Arbor, Mich. (1943)].
18. L. Andrieux, *Ann. Chim.*, **12**, 423 (1929).
19. R. R. Ridgway, U. S. Pat. 2,123,158 (1938).
20. G. H. Fetterley (To Norton Company), U. S. Pat. 2,542,916, Feb. 20, 1951.
21. S. J. Sindeband and R. P. Seelig, Paper on "Fusion Electrolysis Apparatus for the Production of Metal Borides," presented at Washington Meeting of The Electrochemical Society (1951).

Electric Furnace Phosphorus Development

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Fifty years ago the manufacture and uses of elemental phosphorus did not exceed 400 tons a year. Its use was limited to nonferrous alloys, strike-anywhere matches, red phosphorus for safety matches, the manufacture of pure phosphoric acid, and the preparation of pharmaceuticals, principally hypophosphites. Today the installed capacity of electric furnaces for phosphorus manufacture exceeds 190,000 tons (1).

Two significant changes regarding the manufacture and use of phosphorus have taken place over the half-century. First, it has shared in the growth common to all branches of the American chemical industry. Second, elemental phosphorus has replaced phosphate rock and sulfuric acid as the basic raw material in the manufacture of phosphoric acid and phosphate salts of all kinds and, indeed, to a limited extent in the production of fertilizer.

Following a long period (1910–1937) of competition between the electrothermal and pyrolytic (blast furnace) methods, the former, with the development of large-scale furnaces, has demonstrated its economic superiority.

Economic factors such as increasing cost of sulfuric acid, increasing cost of transportation, improvement in burning phosphorus, the use of the Cottrell system for completely collecting the products of combustion together with the large electric furnace, have changed the picture as regards phosphate salts derived from phosphoric acid. The use of phosphate salts has increased enormously during the past ten to fifteen years.

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Between 1870–1880 attempts were made to produce phosphorus in the United States by the chemical pyrolytic method, the same as used in Europe at that time. They were on a very small scale and not very successful. Later phosphorus was manufactured at the Moro Phillip Works at Camden, New Jersey, but until 1897 the principal supply in the United States was imported.

In 1897 Oldbury Electro-Chemical Company commenced manufacture by the electric furnace at Niagara Falls, New York. The company was a branch of Albright and Wilson, Limited, of Oldbury, England, owners of the Readman Parker patent for the manufacture of phosphorus by the electric furnace, a process already operating in England. The furnaces were approximately 100-kw single-phase. An associated company, the Phosphorus Compounds Company, in which Mallinckrodt Chemical Works were also interested, produced phosphoric acid and other pure chemicals from the phosphorus. Manufacture of phosphorus in the electric furnace was started by the American Phosphorus Company at York, Pennsylvania, (1902–1905) and continued until the close of World War I. During the war and preceding it, experimental work was done in the Department of Agriculture in the production of phosphoric acid directly from rock, both by electric and blast furnace methods, with a view to the elimination of sulfuric acid and attaining more concentrated fertilizer (2).

Following the war, Theodore Swann commenced the manufacture of ferrophosphorus and applied the information obtained by the work of Ross, Carothers, and Merz in the De-

partment of Agriculture in the burning of the gases from the furnaces and condensation of the resulting acid.

About the same period the Victor Chemical Works installed a large-scale blast furnace under the direction of Waggaman for the reduction of phosphate rock. The installations of both Swann and Victor gave phosphoric acid, which was more easily purified for food products than that obtained from the sulfuric acid method. These installations also were on a sufficiently large scale to be competitive as regards phosphate for detergents. Both processes could be modified so as to condense all or part of the phosphorus from the gases before burning. Other smaller installations were made of both blast and electric furnaces.

With the inception of the Tennessee Valley Authority, in 1933, experiments were conducted at Wilson Dam, Alabama, on electric furnace production of phosphoric acid, burning the gases directly from the furnace, hydrating, and collecting the acid, and also by condensing the phosphorus and burning it separately at another stage. The work followed lines similar to that of Swann, and T. V. A. developed furnaces for the production of elemental phosphorus. The work done under the direction of H. A. Curtis has been written up most completely by Curtis, *et al.* (3), and in T. V. A. reports. The acquisition of the Swann Company by Monsanto Chemical Company and subsequent building of the plant at Monsanto, Tennessee, for the production of elemental phosphorus, together with the work at T. V. A., proved the superiority of the electric furnace method over the blast furnace. Since 1937 the electric furnace has been adopted by almost all other producers as a source of phosphorus for phosphoric acid, not only for food phosphates but for all phosphate salts.

References

1. *Chem. Eng. News*, **29** (Sept. 1951).
2. William Haynes, "History of American Chemical Industry," Vol. **2**, Vol. **4**.
3. H. A. Curtis, Arthur M. Miller, and J. N. Junkins, *Chem. & Met. Eng.*, "Superphosphate by the Electric Furnace Method," **42** (1945); **43** (1946).
4. William E. Gibbs and Claude K. Deischer, "George Rose," (bibliography), *J. Chem. Education*, **27** (May 1950).

Electric Furnace Ferro-Alloys and Calcium Carbide

Joseph H. Brennan*

The electric furnace ferro-alloy and carbide industries are only a little older than The Electrochemical Society. In the 1890's the discovery of calcium carbide by Willson, the researches of Moissan, and the development of electric furnaces by Heroult, Girod, Stassano, and others were laying the foundations for an industry which was in its swaddling clothes at the turn of the century. Perhaps the first important commercial use of electrothermal methods for alloy manufacture in the United States was the production of copper-aluminum bronzes by the Cowles brothers at Lockport, New York. While their method became obsolete with the introduction of Hall's electrolytic process, it was the forerunner of many other more successful enterprises.

The story of the discovery of calcium carbide by Willson at Spray, North Carolina, in 1892 has been told many times. Less well known is the establishment by James Turner Morehead, the guiding spirit of the Willson Aluminum Company, of industries for the production of ferro-alloys at Holcomb Rock, Virginia, and Kanawha Falls, West Virginia, as well as calcium carbide at Niagara Falls, New York, and Sault Ste. Marie, Michigan. These were all going ventures when The Electrochemical Society was founded in 1902.

The subsequent growth of the electrothermal industries, like the chemical industries generally, has been marked by periods of rapid growth and expansion coincident with the world wars. Further expansion on a very large scale is now taking place in connection with the defense effort and the current enlargement of the steel industry. The increasing use of the electric furnace first introduced in America at the Holcomb Steel Company in Syracuse in 1906 as a tool for high quality steel production has been accompanied by an ever-growing use of alloy steels and demand for ferro-alloys. At the end of 1950 electric steel capacity in the United States approximated 6,000,000 tons annually and ferro-alloys were being produced in the electric furnace at a rate approximating 1,100,000 tons annually.

Early attempts to establish an electric furnace industry for the reduction of iron ores, notably that of the Noble Steel Company at Heroult, California, in 1908–1914, were economic failures but the electric steel industry, based on steel scrap as a raw material, continues to prosper because of the superior quality of its product. Indeed, with the increasing size of furnaces and the flexibility of its operation, it looms as an economic competitor of the open-hearth even for low-alloy or plain-carbon steels. Furnaces nominally rated at 100 tons per heat are in operation and larger units are under construction.

Since electrical energy constitutes one of the prime raw materials of the ferro-alloy industry, all of the early ventures were located at sources of low-cost hydroelectric power. With little hydroelectric power available today, the present expansion of the industry is taking place near sources of coal for steam power, notably in the Ohio valley.

The first products of the ferro-alloy industry in the United States were high-carbon ferrochromium, employed in armor plate production, and ferrosilicon used as a de-oxidizer and in the production of silicon steels for electrical applications. By the end of World War I, the electric furnace was producing silicon metal, low-carbon ferrochromium, ferrotitanium, high- and low-carbon ferromanganese, silicomanganese, silicospiegel, ferromolybdenum, ferrotungsten, ferrovanadium, and a number of lesser alloys including ferro-uranium and the zirconium-ferrosilicons. To these must now be added calcium-silicon, ferrochromesilicon, ferroboron, medium-carbon ferromanganese, ferrocolumbium, ferrotantalum-columbium, and a variety of complex alloys containing silicon, calcium, aluminum, zirconium, titanium, chromium, manganese, and boron which are employed in both iron and steel for deoxidation, nucleation, grain refinement, control of hardening, and for the development of specific properties.

In the early promotion of the calcium carbide industry there

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was a mistaken belief that it would serve as an economical additive to illuminating gas, then extensively employed in household lighting. While it was not adaptable for this purpose, it nevertheless found extensive applications for lighting purposes in homes, farms, miner's lamps, and on the early automobiles. Subsequent growth of the calcium carbide industry came with acetylene welding but, at present, the largest use of calcium carbide is in chemical synthesis for acetaldehyde, acetic acid, vinyl compounds, and synthetic rubber. Acetylene production from other sources such as petroleum, has been a potential threat to the calcium carbide industry but, so far, the electric furnace has been able to hold its own economically.

Two general types of electric furnaces are employed by the ferro-alloy industry, the submerged or smothered arc and the open arc. The latter is usually a tilting furnace whereas the submerged arc type is tapped from a fixed taphole. Ferrosilicon, ferromanganese, high-carbon ferrochrome, calcium carbide, and other ferro-alloys employing carbon reduction are produced in furnaces of the submerged or smothered arc type. The charge, consisting of ores or oxides and carbon in the form of coal or coke, is continuously fed at the top of the furnace and the molten products are intermittently tapped from a taphole at hearth level. Submerged arc furnaces may be single- or three-phase. In three-phase furnaces the electrodes, when rectangular, are usually arranged in line. When round electrodes are employed, a delta arrangement is preferred. Single-phase units of as little as 500 kilowatt capacity to three-phase units of more than 20,000 kilowatts are operated. The larger units are principally used for calcium carbide. Linings are constructed of carbon blocks and the dimensions of the furnaces are such that part of the charge itself constitutes the principal lining of the furnace. Furnaces of this type operate on long continuous campaigns and, except for product changes, may operate for a period of years without lining or hearth repairs.

Developments in this type of furnace have worked toward increasing size of the unit and means of collecting the gases and fumes liberated. All early units of this type were built with open tops which permitted the carbon monoxide evolved to burn at the upper surface of the mix. Complete enclosure of this type of furnace has involved many difficulties. The continuous feeding of mixture which is necessarily coarse to obtain porosity for gas evolution, the requirements for stoking to maintain mixture flow, and the difficulty of maintaining stuffing boxes around very large electrodes, as well as the violent high temperature "blowing" when porosity is not adequate, are some of the problems encountered in covering furnaces of this type. In one modern type, a nearly complete enclosure is effected where the carbon monoxide is collected, washed free of dust and fume and utilized in auxiliary operations, largely for fuel.

Because of the reactance problems involved by very heavy currents in furnace design, the early installations sought 25-cycle power and, indeed, it is probable that the projected needs of the electric furnace industry were a major factor in the decision to make the first hydroelectric installation at Niagara Falls 25-cycle. The almost universal installation of 60-cycle power elsewhere in the country and the need of interlocking power systems has led to design of satisfactory 60-cycle furnaces and the industry as a whole is converting to power at this frequency.

The ferro-alloy and carbide industries in the United States principally use carbon electrodes. Self-baking electrodes of the Söderberg type, while extensively employed in aluminum cells, have had only limited use in the United States for ferro-alloy and carbide furnaces. The Elkem furnace, a submerged-arc design having fixed electrodes and a rotating hearth, is currently being tried by the Tennessee Valley Authority in the manufacture of phosphorus.

An important auxiliary to furnaces of the submerged arc type is the tapping electrode. Here a small graphite electrode connected to the furnace circuit is used to burn out the taphole and facilitate tapping. It is almost indispensible to large carbide furnaces but may be replaced with an oxygen lance in some types of alloy production.

The low-carbon alloys of chromium, manganese, and vanadium cannot be practically produced by refining the high-carbon alloys which result from reduction by carbon. Early manufacture of these metals and alloys was by aluminothermic processes of Goldschmidt. Silicon reduction processes devised by F. M. Becket preceded large and economical manufacture of low-carbon ferrochromium and ferromanganese. He discovered that silicon would exclude carbon from alloys and devised two-stage processes involving carbon reduction for the manufacture of low-carbon silicides of chromium and other metals and used those silicides in a second operation for the reduction of ores and oxides. These processes have been of particular importance in the manufacture of low-carbon ferrochromium as a base for stainless steel. Modifications have led to a steady lowering of the carbon content in commercial ferrochromium until now a product containing less than 0.03 per cent carbon is available in large tonnage. This has been of extreme importance in the developing metallurgy of stainless steels. In France and England semiexothermic processes involving the use of silicides devised by R. Perrin have found application in low-carbon ferrochromium manufacture; these processes have had only transient use in the United States.

Low-carbon ferrochromium, ferromanganese, ferrocolumbium, ferrovanadium, chromium, and manganese metals are produced in furnaces of the open arc type. Here the mixtures, usually ores, silicides, and fluxes, are fed continuously to an open bath where reduction and melting are simultaneous. The furnaces of the Heroult type are basic-lined with structural modifications to take care of the large slag volumes which are produced. Unit furnaces vary from 500 to several thousand kilowatts. Manufacture is a batch operation as in steel making with the furnace being completely tapped and the lining being repaired each heat.

Technological developments have been largely in the field of processes capable of handling the varying ores and raw materials which the industry must necessarily employ. These developments have included new processes for the concentration and preliminary purification by chemical, metallurgical, and mechanical means of tungsten, vanadium, columbium, chromium, and manganese ores. Furnace development has been toward increasing size largely in power input, for in contradistinction to steel metallurgy, the energy required in ferro-alloy production is largely used in doing chemical work of reduction rather than simple thermal melting.

Aluminothermic processes still find application in the specialized manufacture of ferrovanadium, ferrotitanium, ferrocolumbium, and chromium and manganese metals.

New products of the ferro-alloy industry commercialized in the last two decades have included ferrocolumbium, nitrogen-bearing ferrochrome and ferromanganese, a number of

proprietary complex alloys for special purposes, and exothermic alloys. These latter are combinations of ferro-alloys with oxidizing agents and silicon which, when added to molten steel, develop enough energy to melt themselves. They are employed as ladle additions and effect an alloying addition without temperature loss.

No résumé of the ferro-alloy and carbide industries would be complete without reference to the pioneers who made important technical contributions to its growth during its early beginnings in the first decade of the century. These men include Frederick M. Becket, George Cox, Emile Darte, M. Du Chalmot, Franz van Kugelgen, James G. Marshall, James T. Morehead, Edgar F. Price, August Rossi, Byranji Saklatawalla, Frank J. Tone, and Robert Turnbull.

Electric Furnaces in the Iron and Steel Industry

*H. S. Newhall**

As early as 1800, the carbon arc was used by Sir Humphrey Davy. This work, of course, was very primitive but did bring about the beginning of useful application of the electric arc to industry.

Not much further work was done until approximately 1876 when Sir William Siemens constructed some small furnaces using both the direct and indirect arc principle. Electric power at that time was limited and, consequently, the development of the electric furnace was quite slow.

Before the turn of the century, however, considerable work had been done in the development of electric furnaces for aluminum, calcium carbide, ferroalloys, silicon carbide, and graphite. Both Heroult in France and Hall in the United States developed processes for the production of aluminum, ferroalloys, and steel melting.

In 1899 the first direct arc furnace, designed by Heroult, was installed, and in 1900 the first shipment of steel was made from the plant using this furnace. In the next few years, the greatest development in electric furnaces was carried on abroad with most of these furnaces using the bottom contact principle.

In the United States the first arc furnace was installed by Heroult at the Halcomb Steel Company in Syracuse, New York, in 1906. This was a single-phase, two-electrode, rectangular furnace of four tons capacity. Soon after this, other furnaces of rather limited tonnage were installed at the various steel plants in the United States. It is interesting to note that the first furnaces operated on steel for ingots. Not until 1911 was there an electric furnace installed for the production of steel castings.

This is ironical in that the steel casting industry took much greater advantage of the electric furnace in the following thirty years, and during that time the electric steel casting furnace was by far the most prominent and important part of the electric furnace industry. It was not until the second World War that the electric furnace for steel ingots became of paramount importance and, at the present time, the greatest capacity of electric furnaces is going into steel ingots, making the casting industry decidedly secondary in tons produced.

The earlier furnaces were very crude, designed with the simplest means of mechanical operation, selecting one or two voltages, carbon electrodes, door charged, and with various electrical connections that even astound the electrical engineers of today. A most common design on the earlier furnaces included two electrodes with a live bottom; in addition, of course, three electrodes with or without a bottom connection were used and so were two electrodes single-phase. There are still today a few of these older furnaces in operation. Furnaces were powered with very small transformers, and a heat of steel took from eight to twelve hours to produce.

Along with this development in the arc furnace there was a parallel development in the induction furnace. Here again, the induction furnace had its beginning during the nineteenth century. This was first patented by Feranti in Italy in 1877, and in the year 1900 Kjellin designed and operated a single ring furnace in Sweden. Very shortly after this, developments in Germany included more than one ring.

Many unsuccessful operations were carried out between this time and the first World War. Actually, on April 25, 1906, the first heat was rolled and finished into saws from an induction furnace. This is probably the first successful operation of induction furnaces. The greatest development in induction furnaces came when the Ajax Northrup Company developed their high frequency induction furnace, which is still one of the leading induction furnaces.

There have been many other furnaces designed, including resistor furnaces, low frequency induction furnaces, single-electrode arc furnaces, and many others that have all had their try at replacing the present day arc and induction furnaces. However, all of these have dropped by the wayside except in a few isolated instances. For example, the single-electrode, live bottom electric furnace is still used on certain high temperature ferroalloy operations.

This paper is not intended to cover electric furnaces in general but is only to discuss electric furnaces in the steel industry. The best way to cover the history of the electric arc furnace since the first World War is to take the developments and improvements that have been brought forth during these years.

The first step was to increase the powering in the transformer. Whereas the old furnace operated at around 20 to 25 kw/ft^2 of hearth area, the modern furnace operates at from 75 to 150 kw/ft^2 of hearth area, which enables the melter of today to melt down his charge at a fairly rapid rate. Depending upon the size of furnace, the powering, the quality of the steel, and the nature of the charge, the heat time may last from one and one-half hours to five hours or more.

The second most important development in the early stages was the use of multi-voltage transformers. At first, 90 and 100 volts was considered to be a very good operating range but, as furnaces became larger, higher voltages became necessary and operators found that two different ranges of voltages were desirable for melting and refining. It was discovered that the conditions giving the best results, that is, high voltage and high power for melting and low voltage and low power for refining, could be met quite well by connecting the primary of the three-phase transformers in delta for melting and in star for refining. This gave greatly improved conditions for both operations.

* Pittsburgh Lectromelt Furnace Corporation, Pittsburgh, Pennsylvania.

The first electrodes that were used were of carbon. As the years passed, a graphitized electrode was developed which would carry higher amperage. This was more expensive but it was found that the lower cost carbon electrodes were so physically large that the flash from these arcs harmed the sidewalls, and costs of refractories were higher. With the graphite electrode it was possible to group these electrodes closer and bring the arc physically nearer to the center of the furnace, thus cutting down on the arc blaze on the sidewalls. This resulted in longer refractory life, less cost of refractories, and considerable improvements in the economies of steel-melting.

Along with these developments came other minor developments such as water-cooled doors in place of brick-lined doors, water-cooled roof rings, cooling glands to help keep down electrode consumption, water-cooled electrode clamp shoes, together with water-cooled connections to bring the power to the clamp.

As these developments were all brought forward it became obvious that the electric furnace had become a production tool and as such the accounting department was brought in to study this equipment. The immediate reaction was that furnaces were shut down too much. During this shutdown time, the cost of labor and overhead carried on. This forced the electric furnace manufacturers to design ways and means of increasing the load factor.

Through this was developed the top charge furnace. Hand charging of furnaces took from a half-hour to several hours, depending on the size involved, during which time the furnace was standing idle and losing heat. Companies were paying demand charges on their power and, by the use of top charging, the recharging time was cut down to from five to ten minutes.

This development was accomplished quite readily but the accounting department still insisted that the furnace was shut down too much. Studying the problem, it was decided that time could be saved by the use of power-operated electrode clamps in order to cut down the time for slipping and adding electrodes. Today, practically all furnaces built have this feature. These clamps may be spring-held air release, or air-held air release.

The accountants at that time were becoming fairly happy but a condition developed which changed their point of view. Scrap had become light to a point where it was impossible to charge the furnace with one charging bucket. In order to meet this, the furnace manufacturer had to increase the height of the side-plates of his furnace and, as time went on, the furnaces got considerably higher in order to increase the volumetric capacity for scrap. With conditions as they exist today, side-plates may have to go still higher.

As the furnace manufacturer has had to be more strict in his design, he has also made his specifications to the electrical companies more strict. Specially designed transformers are now used which are very heavily braced to stand the sudden shocks involved in melting steel scrap. Motor-operated tap changers now are available so that a minimum of time is used to change from one voltage to another.

The regulator, which was always the bane of the electrician's existence, has now been replaced by one which has considerably less maintenance and, in general, is always accurate. The old style regulators constantly had to be adjusted and high maintenance cost was involved in platinum-irridium contacts.

Circuit breakers, although still not specifically designed for furnace work, are much more adaptable to electric furnace operations. The older circuit breaker, which was normally designed for power transmission lines, was expected to have four or five breaks in a month, whereas an arc furnace breaker is opened and closed a hundred times a day. This put a very heavy strain on the older style breakers and it was not uncommon, many years ago, for breakers to burn out, mainly due to poor maintenance. The present-day breaker, although it still has to be maintained like any other piece of equipment, is designed to withstand these shocks and operate without high maintenance.

The accounting departments are still scratching their heads trying to figure a way to force the American manufacturer to put in under-load tap changers. Actually, at the present time, this is used considerably in Europe but has not found favor in the United States. Here again it is believed the accounting department will eventually win out.

The history of the electric arc furnace in the steel industry is not complete without a short discussion on electric furnaces for the reduction of iron ores. Here in the United States, where coke is inexpensive, the blast furnace has become the standard pig iron production unit.

In countries like Norway, Sweden, Italy, and Switzerland, where no proper blast furnace coke is available and inexpensive power can be generated from the mountain streams, electric smelting of iron ores is carried out to a considerable extent.

Originally, electric pig iron furnaces of 20 and 30 tons daily capacity were in operation. Soon after the second World War furnaces of 50 tons were more or less standard. Today 100 ton furnaces, that is, those capable of tapping 100 tons of pig iron in 24 hours, are considered to be obsolete and furnaces of 150 tons to 200 tons per day are in the making.

As these units develop in size, it may be possible that certain areas in the United States can and will use electric furnace reduction units to furnish a supply of pig iron to the smaller steel plants.

The induction furnace has had a parallel development until today the induction furnace is a highly efficient piece of machinery. As this paper is to cover arc furnace development, it does not seem necessary to go into any great detail with regard to induction furnaces. However, they have their place in industry and will, in the future, be used in their special applications.

Electric Furnaces for Melting of Nonferrous Metals

*G. H. Clamer**

Electric furnaces for nonferrous metals may be grouped under two general classifications, namely:

1. Those in which the heat is transferred to the metal from an outside source.

2 Those in which the electrical energy is converted directly into thermal energy in the metal to be heated due to the resistance of current flow

Group One

Three types of furnaces have come into commercial use: (*a*) overhead arc; (*b*) overhead resistors (metallic and nonmetallic); and (*c*) submerged solid resistors (contained within tubes).

The use of the direct arc, or arc upon a floating slag, was soon abandoned because of metal volatilization.

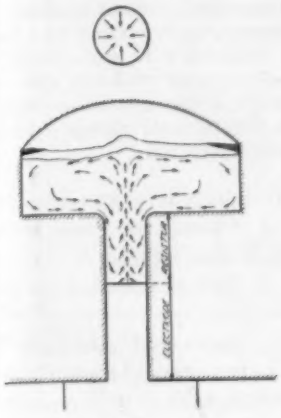

FIG. 1

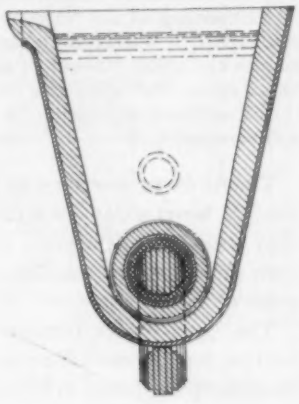

FIG. 2

FIG. 1. Pinch effect furnace showing cross section of a single electrode resistor connected with bath and direction of circulation.

FIG. 2. Ajax-Wyatt submerged resistor induction furnace with u-shaped secondary (Foley type).

The use of the overhead arc type under the name Detroit Rocking Furnace has come into extensive use for melting copper base alloys with relatively low zinc content and for nickel base alloys. The metal in the hearth must be energetically agitated to prevent overheating. This is accomplished by a rocking motion. This type of furnace owes its success to the fact that it is relatively cheap as compared with the high frequency induction furnace and, like that furnace, can be completely emptied. It can, therefore, be used like a crucible furnace for alternate melting of metals and alloys of varying compositions.

Furnaces using external metallic resistors are successfully used for melting the relatively low melting point alloys.

Furnaces using nonmetallic resistors such as Globar are used to a limited extent for melting or holding in the molten state the higher melting point alloys.

Metallic resistors contained within nonmelting tubes submerged in a bath of liquid metal are successfully used for low melting point metals and alloys.

Group Two

Under this group, two general types of induction furnaces have come into commercial use: (*a*) submerged resistor, using normal frequency; and (*b*) coreless induction, using high frequency.

Attempts were made to melt brass in an open ring induction furnace. These attempts were abandoned because of the disruption of the circuit due primarily to "pinch effect."‡ Much effort and money was spent in an endeavor to develop a satisfactory furnace using water-cooled metallic electrodes to supply current directly to a column of liquid metal (Fig. 1). Because of failure to maintain a leak-proof hearth and excessive heat loss due to required water cooling for the electrodes, efforts to produce a commercial furnace were abandoned.

A leak-proof hearth and zero heat loss due to water cooling was accomplished by the simple expedient of abandoning water-cooled electrodes and utilizing "pinch pressure" for circulation in a submerged resistor induction furnace. In a single-phase electrode type "pinch effect" furnace, two columns of liquid metal are short-circuited by the metal in the hearth. To convert such a furnace into an induction furnace it is merely necessary to join these two columns of liquid metal and thread a transformer through the loop which results. The metal in the hearth, as heretofore, serves to complete the circuit (Fig. 2). Due to "pinch pressure" developed in the molten metallic loop the metal therein is actively circulated. The current conditions in respect to the diameter and length of the metallic loop are so proportioned that rapid heating results due to the resistance to current flow. Under correct conditions current density is of sufficient magnitude to produce a decided "pinch effect." Due to the "pinch effect" the liquid metal in the resistor loop is not overheated because the heat is carried out to the bath by metal ejected from the channel of restricted dimensions. The bath in the furnace must be of sufficient depth to prevent actual rupture of the circuit by "pinch pressure." A superimposed bath transfers its added heat units to the solid metal charged therein, melting the same and adding the desired degree of superheat to bring it to the proper casting temperature.

During the course of the experiments with the electrode type "pinch effect" furnace, the late James R. Wyatt discovered that if the molten metallic resistor loop (secondary of the transformer) was to be made angular an additional electromagnetic pressure was superimposed on "pinch pressure" due to motor effect (Fig. 3). The use of a submerged return-bend angular resistor so increased the degree of circulation that such furnaces could be successfully used for melting high zinc content brasses.

This type of furnace was introduced during the first World War under the name "Ajax-Wyatt Induction Furnace." Prior to that time practically all brass in the wrought brass industry was melted in crucibles holding only 200 pounds of metal. The crucibles were made of clay and graphite. No satisfactory domestic clay or graphite was then available. Both were imported and hence strategic materials. After the imported clay and graphite were no longer available, crucible manufacturers diligently attempted to make satisfactory crucibles of domestic clay and graphite. Crucibles made of domestic materials at that time exhibited very short life as compared with crucibles made of imported materials. In the old crucible practice zinc losses were high due to volatilization. It was estimated at that time that the daily zinc loss in the wrought brass industry was 25 tons.

* President, Ajax Electro Metallurgical Corporation, Philadelphia, Pennsylvania.

‡ Term used by Hering to describe the action that takes place when a certain current density is exceeded, viz., the molten secondary is contracted.

The situation became critical just at the time the Ajax-Wyatt furnace was developed to a commercial stage. The first furnace, powered with only 30 kw, was installed at the Bridgeport Brass Company, Bridgeport, Connecticut. The success of the original unit was such as to lead to the complete abandonment of the old crucible practice at that plant and the substitution of Ajax-Wyatt furnaces. They tore down their high stacks, so necessary not only for creating the proper draft for the fuel-fired furnaces used but also for carrying off into the high atmosphere the voluminous zinc oxide produced. The Bridgeport Brass Company advertised extensively that henceforth they would produce only electric furnace brass. A large illuminated sign on their plant has for many years been visible to the passengers on the New York, New Haven & Hartford trains. Shortly thereafter The American Brass Company installed a furnace powered with 60 kw. The step up from 30 kw to 60 kw presented new refractory problems.

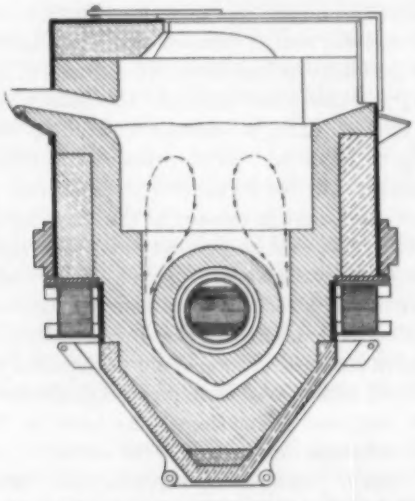

FIG. 3. Ajax-Wyatt submerged resistor induction furnace with v-shaped resistor showing direction of metal circulation.

These, fortunately, were overcome without too great a lapse of time and The American Brass Company also, step by step, substituted induction furnaces for crucibles. With success of the induction furnace established by these two large units of the wrought brass industry, adoption rapidly proceeded until today almost 100 per cent of crucible melting has been abandoned for Ajax-Wyatt furnaces.

The size of the submerged resistor induction furnace has been steadily increased over the years: from the original 30 kw furnace to 60 kw, to 150 kw, to 300 kw, and recently to 1,000 kw. The thousand kilowatt furnace is equipped with three inductor units of 333 kw each and exhibits melting rate of 10,000 pounds per hour. It has a hearth holding capacity of 20,000 pounds. A modified type of Ajax-Wyatt furnace was developed by the joint efforts of the Scovill Manufacturing Company, The Scomet Company, and Ajax Engineering Corporation (Fig. 4). The following is a quotation from an article by L. P. Sperry, President, Scovill Manufacturing Company, Waterbury, Connecticut, appearing in *Iron Age*, December 22, 1949:

"Outstanding among the innovations at the new Scovill mill are the 5-ton per hr induction melting furnaces, shown in the accompanying illustrations, which feed hot metal to the continuous casting machine. These Ajax-Scomet furnaces, of which two are already installed and another under way, are the largest used for melting brass.

"These furnaces, built by Ajax Engineering Corp., under Scomet license, are of the drum type, with a rated capacity of 1000 kw each. Power supply is 575 v, 60 cycle three-phase, with all phases balanced. Each furnace has a melting capacity of about 10,000 lb per hr, presently being discharged in 5000 lb lots at staggered 30-min intervals. Precision control of melting temperatures is automatic, with permanently inserted thermocouples and high-low change of power.

"Construction of the furnace, shown in the accompanying sketch, consists of an octagonal steel drum (A) provided with a refractory lining (B) of prefired shapes and standard bricks. Three detachable inductor units (C, D, E) each rated at 333 kw, are attached to the lower side of the drum, generating heat in the melting channels (F, G, H, K). The melting channels form two secondary loops, interlaced with two primary coils (L, M), acting as secondary winding of a short-circuited transformer. The two primary windings surround a closed transformer coil (N).

"The inductor units can be readily detached and replaced without interrupting operation of the furnace. This is accomplished by rotating the drum to bring the inductor requiring changing above the molten metal line, thus discharging the inoperative inductor while keeping the metal heated with the two remaining inductors. Each inductor unit has two blowers (O) for cooling the transformer core and primary windings.

"Efficiency of the furnaces, according to present experience at Scovill, is higher than that obtained with any other type, due to the great amount of power concentrated in a relatively small space. Metal holding capacity of the furnace has been reduced as much as possible to facilitate rapid change of alloys, a considerable factor in brass mill operation."

The furnaces described by Mr. Sperry have now been operated 24 hours a day for a period of about two years. During that period of operation a tremendous tonnage of brass has been melted under conditions of absolute precision and with great economy.

The Ajax-Wyatt furnace has been used principally for melting copper base alloys used in the wrought brass industry. Some have been used in foundries engaged in large production of castings of a single alloy or a few alloys, all of which can be modified in composition from a base alloy. Some have been used for melting zinc and recently installations have been made in the ferrous field.

A modified form of the Ajax-Wyatt is finding very extended use for aluminum melting. It is known as the Ajax-Tama-Wyatt furnace (Fig. 5). The use of the submerged resistor induction furnace for melting aluminum was delayed for many years because it was found that the channels of the secondary circuit became rapidly incrusted with aluminum oxide. The incrustation takes place even though the surface of the bath is protected by a reducing medium. The reason for the incrustation has never been satisfactorily explained. The incrustation builds up rapidly and in so doing restricts the cross section of the molten aluminum secondary. With the reduction in the diameter of the secondary the tendency to be ruptured by "pinch pressure" increases until it is finally ruptured, thus breaking the secondary circuit.

Attempts were made to clean the secondary channel by means of articulated tools. Another means for cleaning the channels was to empty the furnace through a bung-hole so located that a tool could be inserted after the furnace was emptied. This method of cleaning was unsatisfactory from the standpoint of efficient operation. It was only after so designing a furnace that the incrustation could be removed from the secondary channels without emptying the furnace, by means of a straight tool; a really successful furnace resulted. Ajax-Tama-Wyatt furnaces have come into very extended use because of their cleanliness, a minimum of heat dissipation into surrounding atmosphere, accurate temperature and alloy composition control, and reduced metal loss.

Another type of induction furnace is the coreless type. These are usually operated with high frequency current. The

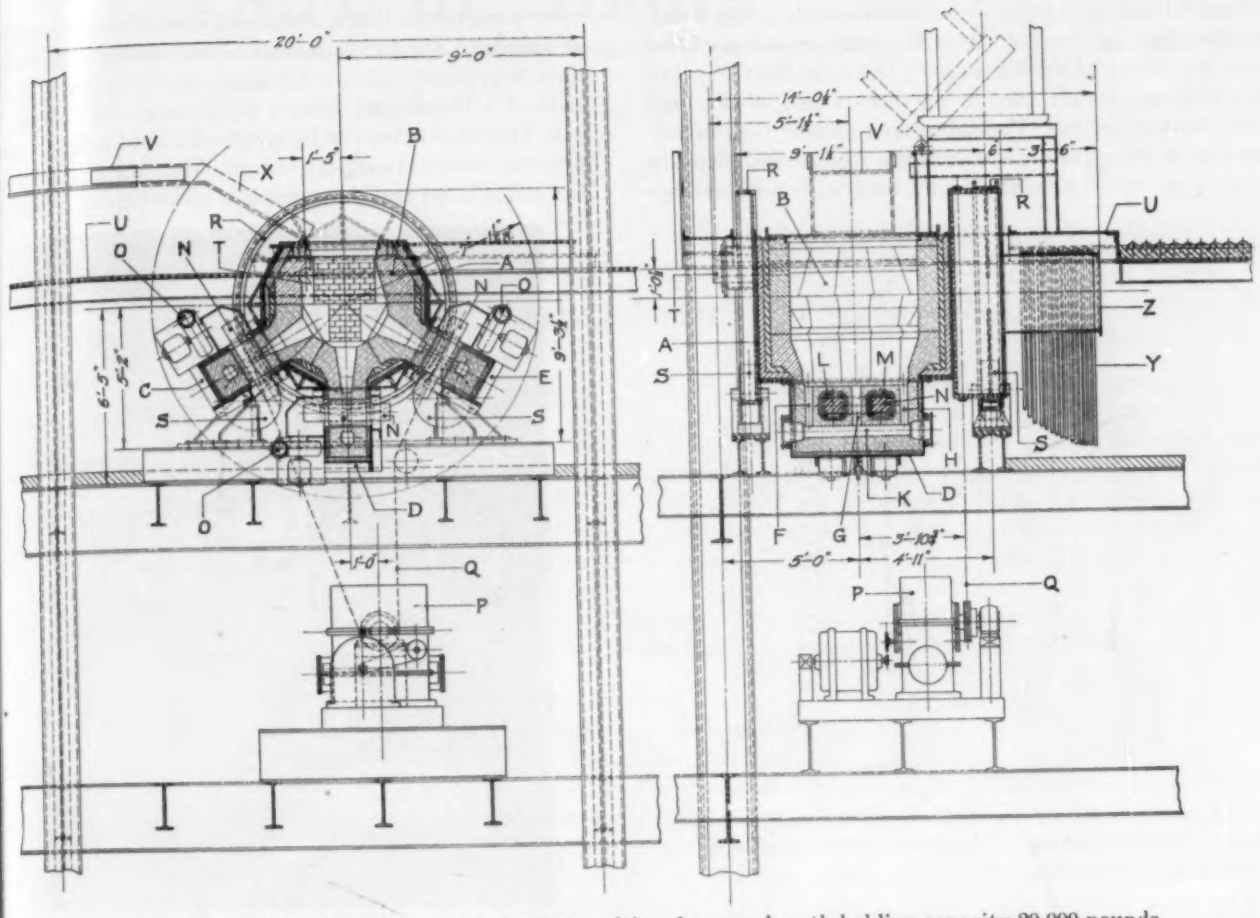

FIG. 4. Ajax-Scomet 1000 kilowatt induction melting furnace, hearth holding capacity 20,000 pounds

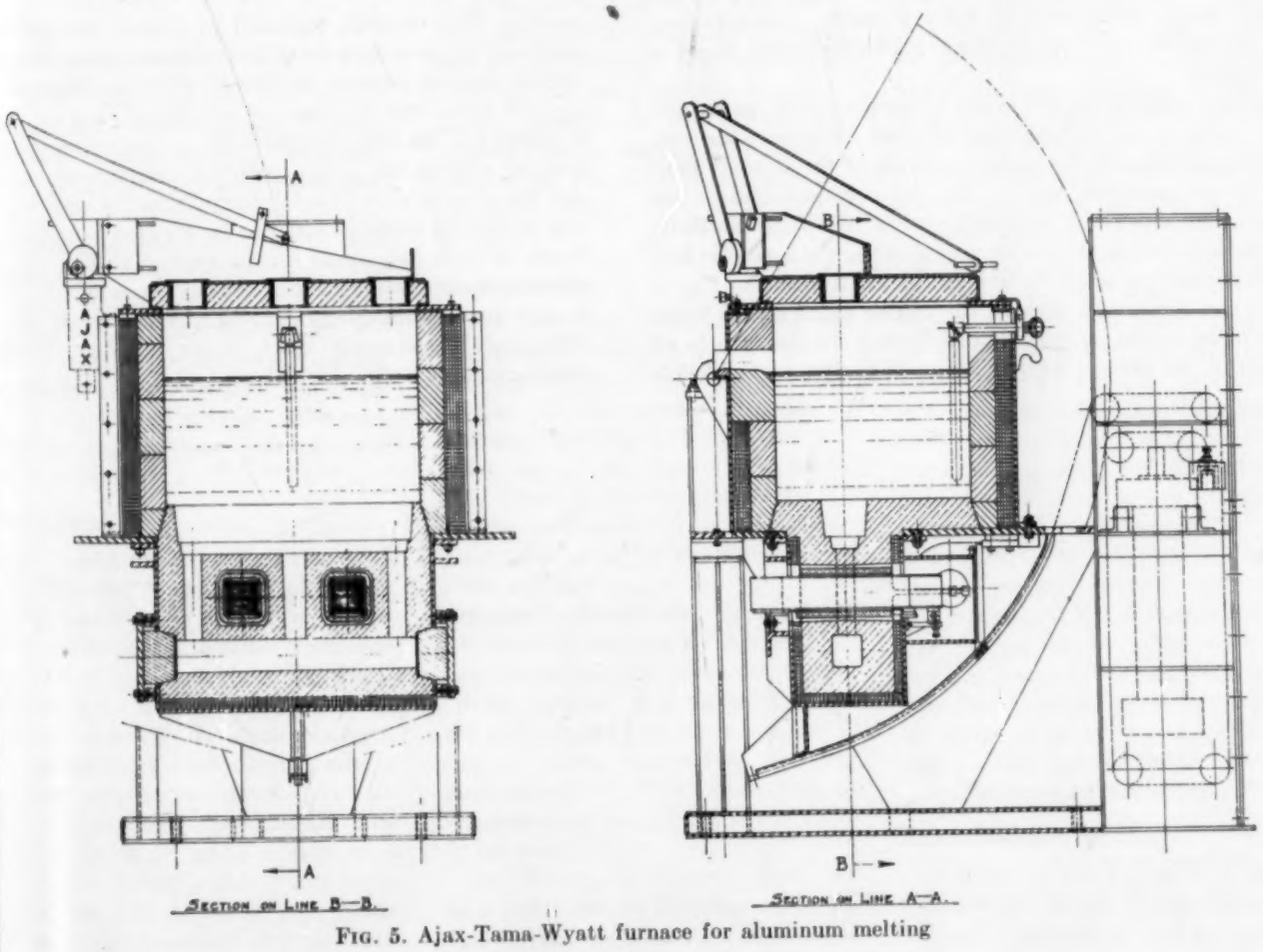

FIG. 5. Ajax-Tama-Wyatt furnace for aluminum melting

original furnace, and the one almost exclusively in use today, was developed by the late Edwin F. Northrup and marketed under the name "Ajax-Northrup." The Ajax-Northrup furnace, although mainly used in the ferrous field, is also used in the nonferrous field. The submerged resistor type of furnace has its principal drawback in the requirement that the metal in the resistor channel and a bath with sufficient hydraulic head above it must be kept continuously molten, or for intermittent operation poured, and the furnace re-started with molten metal from an exterior source. The Ajax-Northrup furnace does not require a molten secondary to act as a resistor.

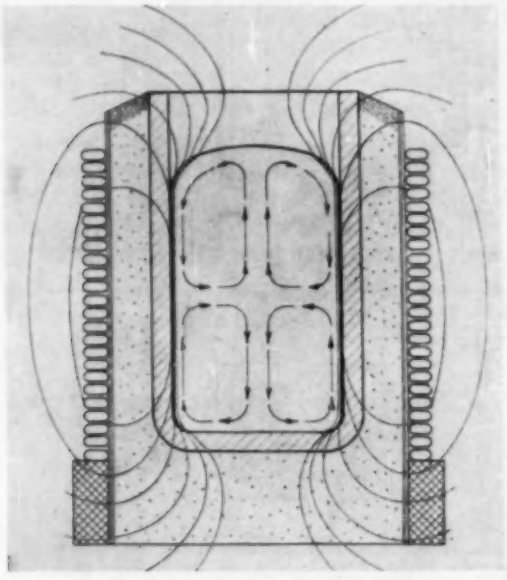

FIG. 6. A sectional view of Ajax-Northrup high frequency induction furnace showing the magnetic field and stirring action of the molten charge.

The hearth or crucible of the furnace is usually cylindrical in shape and can be completely emptied. Because of the complete emptying of the molten contents of the furnace, flexibility of operation results; viz., no contamination of the individual charge. A sectional view of the Ajax-Northrup high frequency induction furnace, showing the magnetic field and stirring action of the molten charge, is shown in Fig. 6. The electromagnetic force in the molten metal charge keeps the metal stirred up, quickly distributing the elements to all parts of the charge, insuring alloys of perfect homogeneity.

In large production a stationary crucible is preferred, but in foundries devoted to making small castings a lift coil furnace is preferred. Such a furnace is shown in Fig. 7. It consists of a box-shaped furnace shell containing the inductor coil. This shell is lowered by means of a hoist around a standard crucible containing the charge. When the melt is finished the coil is lifted and the crucible is picked up on a shank for

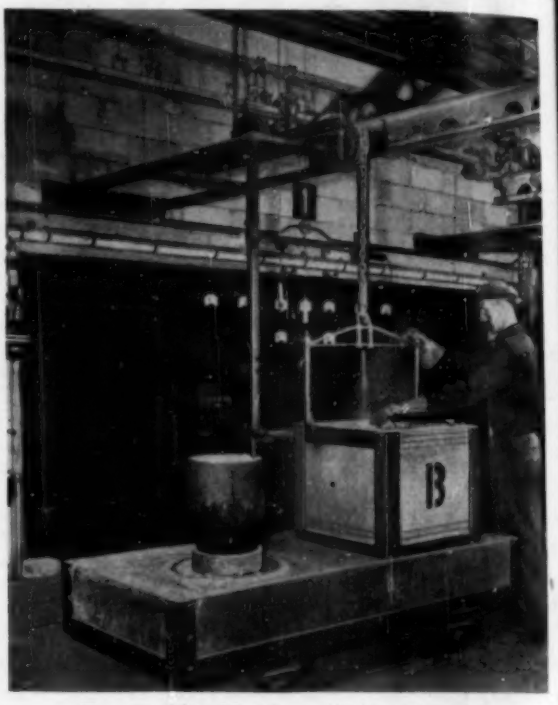

FIG. 7. Ajax-Northrup lift coil furnace

pouring. Two crucibles mounted on a truck arranged with end stops makes a convenient and efficient arrangement. The outside crucible receives its charge while the charge in the crucible within the inductor coil is melting. After the charge is melted and has been brought to the proper degree of superheat for casting, the jacket, with the inductor coil, is lifted and the crucible with its solid charge is moved into the position where the inductor coil can be lowered to embrace it. Power of such magnitude can be applied to the induction coil as to make possible melting time as low as 20 minutes for a red brass mixture. Many Ajax-Northrup furnaces, of both fixed crucible type and lift coil type, are in commercial operation for melting copper base alloys.

Current Affairs

Anniversary Meeting Expected to Set Record

Plans for the Fiftieth Anniversary Meeting of the Society, to be held in Philadelphia, May 4th through 8th, are nearing completion, according to General Chairman Hiram S. Lukens and Publicity Chairman Albert A. Ware. The Benjamin Franklin Hotel, Ninth and Chestnut Streets, will be headquarters for the convention which is expected to attract a record attendance.

Board and committee meetings are scheduled for Sunday, May 4th, and technical sessions will begin Monday morning, May 5th. The registration desk, will be open on Sunday evening from 7:30 until 10:00 P.M., and during the day on Monday through Thursday.

Technical Program

The technical program will include sessions on Electric Insulation, Electrothermics, Instrumentation, Luminescence, Methods of Applying Phosphors, Rare Metals, and Theoretical Electrochemistry. An added feature will be a special round-table discussion on "The Teaching of Electrochemistry." Chairmen of the various symposia are enthusiastic about the number and quality of papers to be presented, and the round tables being arranged. The complete technical program will appear in the April JOURNAL.

Plant Trips

Once again, war is interfering with the traditional program of the Society's convention. Because of security regulations, it has been impossible to arrange for trips to those plants in the Philadelphia area which would be of the greatest interest to electrochemists. It has therefore been decided not to schedule any formal plant trips. In case any of those attending the convention desire to make a visit to a particular factory, the Plant Trip Committee will do all in their power to make the necessary arrangements. It is suggested that members write in advance to the chairman of the committee, Milton P. Barba, % Leeds & Northrup Company, 4901 Stenton Avenue, Philadelphia 44, naming the plant and department they would like to visit, and, if at all possible, the necessary permission will be obtained.

Luncheons

The noonday hour on Monday, May 5th, and Wednesday, May 7th, is being reserved for Divisional Luncheons, the complete schedule of which will be announced later. On Tuesday, May 6th, there will be a General Luncheon, to which the ladies are invited. The speaker on this occasion will be William Page Harbeson, John Welsh Centennial Professor of History and English Literature, of the University of Pennsylvania. Professor Harbeson is one of the most popular speakers in the Philadelphia area and has a wealth of interesting material on the early history and development of the City of Brotherly Love.

Entertainment

The President's Reception and Annual Banquet will be held on Tuesday evening, May 6th. President Ralph M. Hunter will deliver the Presidential Address, Past President Lawrence Addicks, one of the founding members, will speak on the early days of the Society, and the annual Society prizes, Young Author's Prize and Turner Book Prize, will be awarded.

Following the banquet, a general get-together and "community songfest" has been arranged. By popular request, "Sweet Adeline" will be barred from the program. Any members desiring to sing solos are requested to file their applications with the Entertainment Committee at least 24 hours in advance of the event.

On Wednesday evening, there will be a buffet supper, following which the Entertainment Committee has arranged a program of entertainment which will be fully up to the Philadelphia standard. Once again, for security reasons (the Committee's security, that is) details cannot be given in advance. Suffice it to say that it is a program in which every conventioneer will participate and which is guaranteed to give complete relaxation from the heavy mental strain of the day's technical sessions.

Ladies' Events

The Ladies' Committee, under the chairmanship of Mrs. Russell P. Heuer, will see that the feminine portion of the convention is kept occupied during those hours when the men are busy at the scientific sessions. At 11 o'clock on Monday morning, May 5th, there will be a "Kaffee-Klatsch" where everyone can get acquainted and make arrangements for visits to points of historical interest, shopping centers, etc. It is hoped that in this way the visitors can see those features of Philadelphia which are of greatest interest to them. As technical sessions will be held on Monday evening, there will be a card party for the ladies at that time.

On Wednesday, May 7th, there will be a trip by bus to the Huntingdon Valley Country Club for luncheon, at which Mrs. Blanche Scarlett Phelps, one of the country's leading authorities on flower arrangement, will give a talk on that subject. After lunch, a visit will be made to the Bryn Athyn Cathedral. This outstanding example of ecclesiastical architecture and landscaping, which has been under construction for over twenty years, is the work of a resident group of artisans and artists who produce in the adjoining workshops all of the stone and wood carvings, as well as the stained glass, used in its construction and ornamentation.

Historical Exhibit

A feature of the Philadelphia meeting will be the exhibit of apparatus and industrial equipment used in the early

days of electrochemistry. The committee has received the loan of a number of noteworthy items. If any members have such exhibit material to add to this loan collection, they should write to the chairman, Arthur Osol, Philadelphia College of Pharmacy and Science, 43rd and Kingsessing Avenue, Philadelphia 4, Pa.

Hotel Reservations

Indications are that the Fiftieth Anniversary meeting will be one of the largest, if not the largest, conventions in the history of the Society. It is therefore recommended that those planning to attend should make their hotel reservations as early as possible. Write directly to the management of the Benjamin Franklin Hotel, Ninth and Chestnut Streets, Philadelphia 5, Pa.

DIVISION NEWS

Electronics Division

Nominations for officers for the coming year have been submitted by the Nominating Committee of the Electronics Division. The election will take place at the Spring Meeting in Philadelphia. The slate is as follows:

General Chairman of the Electronics Division—J. R. Musgrave, The Eagle-Picher Company, Joplin, Mo.

Vice-Chairman for Rare Metals Group—D. M. Wroughton, Westinghouse Electric Company, Pittsburgh, Pa.

Vice-Chairman for Luminescence Group—A. L. Smith, RCA Victor Division, New Holland Pike, Lancaster, Pa.

Vice-Chairman for General Electronics—M. Sadowski, Philco Corporation, Lansdale Tube Plant, Lansdale, Pa.

Secretary-Treasurer—C. W. Jerome, Sylvania Electric Products Inc., Salem, Mass.

H. C. Froelich, *Chairman*

SECTION NEWS

Chicago Section

The Chicago Section met on January 4th, at the Chicago Engineers' Club. Following the dinner, Ivan C. Blake, Research Engineer, Burgess Battery Company, Chicago, addressed the group on the subject "A Decade of Primary Battery Development."

Mr. Blake emphasized the tremendous progress achieved in primary batteries from the standpoint of (1) shelf life, (2) capacity per unit volume and weight, and (3) the goals to which present research is directed. By showing the status of each of the several types of primary cells at various times during the past ten years, Mr. Blake was able to extrapolate to the quality anticipated in the next few years.

The speaker's assistant, Louis D. Foust, presented each member of the audience with samples of the various types of cells as each was being discussed. Also, each member of the audience received a pocket flashlight powered by a pair of No. 7 cells (Burgess, of course).

* * *

At a previous meeting, held on December 7th, J. P. Casey, Jr. addressed the members and their guests on the subject "Corrosion as a Factor in Design."

Mr. Casey has been engaged in corrosion work for the past ten years, and is at present in charge of the Chemistry and Physics Section of the Engineering Laboratories of the Crane Company, Chicago. In his talk he gave specific information required to make an accurate selection of materials for various uses. Factors such as temperature, velocity of flow, etc., were taken into account as well as the physical and chemical properties of the metal involved.

Howard T. Francis, *Secretary*

Detroit Section

A joint meeting of the Detroit Section of The Electrochemical Society and the American Electroplater's Society was held on January 4th, at the Hotel Statler, Detroit.

Ralph A. Schaefer, Cleveland Graphite Bronze Company, Cleveland, spoke on "Some Practical Considerations of Current Distribution." Dr. Schaefer brought a combination of practical experience and technical insight into his discussion of the problems and his listeners were treated to an expert analysis of the subject.

A. M. Linn, *Secretary-Treasurer*

New York Metropolitan Section

"Zirconium, Its Past and Possible Future" was the subject of an address by William M. Raynor of the Foote Mineral Company, Philadelphia, before the New York Metropolitan Section, at its January 23rd meeting.

Mr. Raynor has been in touch with the various stages in the manufacture of zirconium, including research, development, and marketing. He began his talk with a review of the history of zirconium, pointing out that it is not by any means rare—zircon sands occur on almost every beach—but that its metallurgy is very difficult. The processing of zircon ($ZrSiO_4$) to soluble salts was considered; this is practically the only commercial source, since South American deposits of zircite (ZrO_2) have not proved economical.

The first commercial zirconium metal was a powder produced by Foote Mineral Company, he said, beginning in 1930, by the magnesium reduction of ZrO_2. This powder was useful in pyrotechnics, photoflash formulations and the like, but was too pyrophoric for general application and attempts to work it up into ductile metal by powder metallurgy techniques were not successful. This product is still made, calcium now being used instead of magnesium for reduction.

The manufacture of ductile metal awaited the perfection of the de Boer-van Arkel iodide process, Mr. Raynor stated, patents for which were purchased by Foote. A project was sponsored at Battelle Memorial Institute with the aim of transferring this process from small-scale glassware to more commercial equipment, and in 1945 the Foote Mineral Company offered ductile zirconium at the initial price of $650 per pound.

Mr. Raynor pointed out that the Kroll process (magnesium reduction of the tetrachloride) now competes with the iodide: it is cheaper, but so far has not produced as good a grade of metal.

Ductile zirconium has many interesting properties, the speaker said, including good corrosion resistance (better in general than titanium) and extremely high sensitivity to gases which makes it useful as a getter. Volumetrically, it is about as expensive as tantalum, to which it is superior in resistance to alkalies though not so good against acids. Its high-temperature properties are not outstanding.

Commercial zirconium contains about 2 to 3 per cent of its sister metal hafnium; when the hafnium is removed, the resultant pure zirconium has interesting possibilities in the atomic energy field.

The present status of the zirconium market, the speaker said, seems to be that a metal with some very promising properties and potentialities is available, but the price is still high (about $110 per pound for iodide and $30 for Kroll-process) and no very large-scale applications are predicted for the immediate future.

The speaker concluded by describing the machining and handling of iodide zirconium, and exhibited many interesting samples, including actual "hairpins" of zirconium and titanium, a sample of pure hafnium, various articles of zirconium such as sheet and wire, and a sample of iodide silicon. The iodide process is, of course, capable of application to many elements, and the silicon made by this method promises applications in the field of semiconductors, comparable in some respects to germanium.

A large turnout kept the speaker on his feet for some time answering questions. Of particular interest was discussion offered by Dr. W. C. Lilliendahl, a pioneer in the rare metals field.

F. A. Lowenheim, *Secretary-Treasurer*

Niagara Falls Section

On January 15th, Dr. Ralph M. Hunter, president of The Electrochemical Society, spoke before a joint meeting of the Niagara Falls Section of the Society, and the Western New York Section of the American Chemical Society. His topic, "What the Pioneers Missed," was enthusiastically received by an unusually large audience.

An abstract of Dr. Hunter's talk follows:

The pioneers of electrochemistry, as exemplified by Beckett, Burgess, Dow, Fitzgerald, Acheson, and Tone, discovered vast fields and established great and useful industries. The growth of the processes they developed is ample proof of their scientific and economic soundness. Their manufacturing facilities were simple, and they changed them each time they discovered a new fact. In the majority of cases improvements were made by those who followed, and in some cases the processes are successful because of skillful avoidance of unsolved technical problems. From experience with several processes established by the pioneers, the speaker suggests that many explanations are lacking for various phenomena successfully used.

Castner's mercury cell operates very much as Castner conceived it, except for benefits received from improved materials, but many of the difficulties he encountered are still unsolved. LeSeur's alkali chlorine cell with asbestos diaphragm still operates with reasonable success. A vast improvement in it was made by the Hooker Company's drawn diaphragm, but many of the data required for mathematical solution of its behavior are lacking. In electrolytic magnesium production cathode behavior is still mysterious, and the difficulties are avoided but not solved. How then does such a backward group of industries, although mature, continue to grow as rapidly as many younger industries?

The electrochemical industries are too well adapted to grow by small-step experimentation. The units are small and relatively inexpensive. Experiments are cheap. The electrochemical section of a $20,000,000 chlorine plant can be steadily improved by a series of experiments involving less than $10,000 worth of its equipment and at the risk of losing less than $100 worth of product per day. However, if a few tubes in one of its boilers or if one of its evaporators should need extensive repairs, the product loss is enormous and $10,000,000 worth of equipment stands idle.

It would appear that the best literature and published engineering data are found in those industries in which large units are used and generally purchased, whereas, the men who develop their own equipment are neither required, nor encouraged, to publish and develop extensive engineering formulae.

Electrolytic chlorine's scientific growth through 55 years of economic struggle, accentuated by a brief flash as a military weapon, is certainly primitive compared with the so-called atomic weapons, where successful plants exceeding our largest in magnitude are designed on a few micrograms of material, or an observation of a few degrees of temperature rise.

Yet, since their birth, the output of chlorine, aluminum, magnesium, electric steel, graphite, and other electrochemical products has doubled about every seven years.

H. R. Oswald, *Secretary*

Philadelphia Section

The Philadelphia Section held its second meeting this season on January 9th at the University of Pennsylvania. Members and guests of the Society met the guest speaker, Dr. Britton Chance, at an enjoyable dinner gathering held at the Lenape Club prior to the meeting.

Dr. John F. Gall, Section Chairman, introduced Dr. Britton Chance, Director of the Johnson Research Foundation, University of Pennsylvania. Dr. Gall pointed out Dr. Chance's versatile background including chemistry, electronics, and biology, and that he is also inventor of an automatic ship-steering

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mechanism. Dr. Chance is well known for his work in enzyme chemistry and in particular for having developed methods for measuring the kinetics of rapid enzyme reactions.

Dr. Chance spoke on the subject, "The Mechanism of Enzyme Action." Horseradish peroxidase, he said, which can be obtained as a stable crystalline enzyme, is an effective catalyst for the oxidation of many organic molecules by hydrogen peroxide. The absorption spectrum of the system changes during the reaction as the enzyme forms complexes with hydrogen peroxide.

Dr. Chance described instrumentation which he has devised for the simultaneous measurement of light

BRITTON CHANCE

intensity at two wavelengths and the oxidation potential in a "rapid flow" apparatus. By this method, at least two porphyrin-H_2O_2 complexes have been detected during the reaction whose half-life is a few milliseconds. Information concerning rate constants for consecutive reactions was interpreted with the aid of an analogue computer, also designed by Dr. Chance. Two one-electron steps are indicated by magnetic susceptibility measurements, the second step being rate-determining. The techniques, the speaker said, are being extended to oxidation systems which involve cytochromes and nucleotides in living cells.

Following the talk, the 40 or 50 persons in attendance were invited to visit the laboratories of the Johnson Research Foundation. Small groups were formed, and the members of the staff gave very interesting expositions of the various phases of the work being conducted. High spots were, of course, the kinetics apparatus and the analogue computer used in the reaction rate studies, and also, stereoscopically projected pictures taken by Dr. Thomas F. Anderson with the electron microscope.

(The abstract of Dr. Chance's talk was prepared by John E. Baer. An abstract of Mr. Snowden's talk, given before the Philadelphia meeting of November 7th and appearing in the January JOURNAL, was prepared by R. D. Eanes.)

EDGAR L. ECKFELDT, *Secretary*

Washington–Baltimore Section

A very interesting panel discussion on the "Electrowinning of Metals" took place at the December 20th meeting of the Washington-Baltimore Section, at the National Bureau of Standards.

This program was arranged by R. S. Dean of the R. S. Dean Laboratories and included, besides himself, talks by Oliver C. Ralston and David Schlain of the U. S. Bureau of Mines.

Mr. Ralston reviewed the development of methods for electrowinning of zinc, starting during World War I with no production and coming to the present time when two-thirds of the supply is produced by electrowinning. He pointed out that the higher purity of the electrowon product justified the higher cost when purity was important. He also described a recent development by Glen Ware at the Albany Station, which will make it possible to use cathodes at least two weeks before stripping whereas now this has to be done each day. This can be accomplished by simply reducing the level of the electrolyte a small amount each day and thereby reducing corrosion at the electrolyte level.

Dr. Schlain described his work in developing methods for refining antimony in the presence of gold and silver. He was able to obtain an efficiency of 99 per cent with a bath containing 84 g/l of $SbCl_3$ and 53 g/l of H_2SO_4 at a current density of 6 amp/ft.^{2} By using a more concentrated $SbCl_3$ solution he was able to increase the current density to 20 amp/ft.^{2}

Dr. Dean briefly reviewed the development of, and the present status of, the electrowinning of chromium and manganese.

* * *

The January 17th meeting of the Section was held at the National Bureau of Standards and was devoted to the subject of "Batteries." Samuel Eidensohn, of the Bureau of Ships, Navy Department, as chairman for this program, introduced the two speakers. D. T. Ferrell, Jr., of the Naval Ordnance Laboratory and Frank Solomon of the Yardney Laboratories, Inc., New York, N. Y.

Dr. Ferrell discussed some of his recent work dealing with the reactions of the dry cell which had been carried out at Duke University, and then reviewed the more or less accepted ideas of what constitutes the reactions which take place in a dry cell both during stand and discharge.

Mr. Solomon described as well as illustrated the characteristics of the only new storage battery that has been developed in many years. This battery uses the well-known couple between silver oxide and zinc and was first made practical by André in France, after many had tried and failed. This cell is now being further developed and manufactured by the Yardney Electric Corporation in this country as well as in Europe. The cell, while somewhat limited in life, is capable of capacities up to 50 whr per pound at high discharge rates. Mr. Solomon indicated that a number of problems must be solved before the capabilities of this battery can be fully utilized.

An interesting discussion period followed each of the above talks.

J. C. WHITE, *Secretary-Treasurer*

PERSONALS

RAYMOND F. LEDFORD is now employed at Sunbeam Corp., Chicago, as superintendent in charge of finishing. Mr. Ledford was formerly with Hanson-Van Winkle-Munning Co., Chicago.

HENRY A. STROW has resigned as chief chemist of MacDermid, Inc., Waterbury, Conn., to become president of True Brite Chemical Products Co., Oakville, Conn.

DONALD C. GERNES has joined the research staff of the Kaiser Aluminum and Chemical Corp., Permanente, Calif., as staff engineer (chemical).

F. H. EDELMAN has left the International Resistance Co., Philadelphia, Pa., to accept a position as technical director of Electronic Devices, Inc., Brooklyn, N. Y.

P. A. PORECHA, who had been located in Bombay, India, is now at Tata Chemicals Ltd., Mithapur, Saurashtra Rly., Okhamandal, India.

FRANK C. SMYERS has been promoted to assistant manager, from assistant to the superintendent, at U.S.S. Lead Refinery, Inc., Hammond, Ind.

EMERY MESCHTER has been made Research Manager of the Parlin Laboratory of the Photo Products Department, E. I. du Pont de Nemours & Co., Inc.,

Parlin, N. J. Mr. Meschter was previously located at the company's plant in Towanda, Pa.

C. H. CHAPPELL, National Carbon Co., has been transferred to the New York office, Electrode Sales Division, at 292 Madison Ave., where he is in charge of the Technical Sales Service and Development Department. Mr. Chappell was previously in the Niagara Falls plant as electrothermic engineer in the Electrode Service Engineering Department.

JOHN G. DEAN is now a chemical research consultant with headquarters at 8 Beaumont Circle, Tuckahoe, N. Y. He was formerly with The International Nickel Co., in charge of the Industrial Chemicals Section, Development and Research Division.

R. M. BURNS has been named Chemical Coordinator in addition to his duties as Director of Chemical and Metallurgical Research at Bell Telephone Laboratories. Dr. Burns has been associated with the chemical activities of the Laboratories since 1922.

ARNOLD D. ARNAUT has left Sylvania Electric Products Inc., Bayside, N. Y., to become associated, as a sales engineer, with the Eastern Sales Division of the Denver Equipment Co., New York, N. Y.

JOSEPH E. DRAPEAU, JR., has left Metals Refining Co., Hammond, Ind., to join the Glidden Co., also of Hammond.

CLYDE A. CROWLEY of Graham, Crowley & Associates, Inc. Chicago, received from the Department of the Army a Certificate of Appreciation for patriotic civilian service during World War II, and specifically for his services on the technical industrial intelligence committee of the Joint Chiefs of Staff. The award was made on January 16th.

ADOLPH BREGMAN

Adolph Bregman, consulting engineer and metallurgist, died at his home in New York City, on October 4, 1951. He was 61 years old.

Mr. Bergman was a former managing editor of *The Metal Industry*, and had been executive secretary of the Masters' Electro-Plating Association since 1933. He was the author of many articles in technical and industrial fields, and was co-author of the text "Finishing Metal Products." He had been a member of The Electrochemical Society since 1941.

NEW MEMBERS

In January 1952 the following were elected to membership in The Electrochemical Society:

Active Members

RICHARD S. BAXTER, Socony Vacuum Oil Co., P.O. Box D., Trenton, Mich. (Corrosion)

ALAN G. CATERSON, Westinghouse Electric Corp., mailing add: 611 Springfield Ave., Cranford, N. J. (Electronics)

PAUL P. CHEVIS, General Motors Truck & Coach Division, mailing add: 2439 Ridge Rd., Pontiac 17, Mich. (Electrodeposition)

WILLIAM C. COCHRAN, Aluminum Research Labs., New Kensington, Pa. (Electrodeposition)

DWIGHT E. COUCH, Chemical Bldg., Rm. 114, National Bureau of Standards, Washington 25, D. C. (Electrodeposition)

BRAM C. FELDMAN, General Electric Co., mailing add: 171 Genesee Park Dr., Syracuse 3, N. Y. (Electronics)

HELLMUTH FISCHER, Siemens & Halske AG, Postschliessfach 497, Karlsruhe/Baden, Germany (Corrosion, Electric

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JOHN S. GERRARD, Kuwait Oil Co., mailing add: 10, 9th St., North, Ahmadi, Kuwait, Persian Gulf (Corrosion and Theoretical Electrochemistry)

JOHN A. GURKLIS, Battelle Memorial Institute, mailing add: 41 W. Frambes Ave., Columbus 1, Ohio (Corrosion, Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

TOSHIO ISHINO, Osaka University, Faculty of Engineering, 9-chome, Higashinoda machi, Miyakojima ku, Osaka City, Japan (Battery, Corrosion, Electrodeposition, Electrothermic, Industrial Electrolytic, and Theoretical Electrochemistry)

WILLIAM G. JAMES, General Electric Co., mailing add: 2412 Malden Rd., Cleveland 21, Ohio (Electronics)

JATINDER KAPUR, D.C.M. Chemical Works, P.O. Box 1211, Delhi, India (Electrothermic and Industrial Electrolytic)

DONALD E. RITZEMA, Dow Chemical Co., mailing add: 40 Rosemary Ct., Midland, Mich. (Electrodeposition)

STANLEY E. ROHOWETZ, Bjorksten Research Labs., Inc., mailing add: 323 W. Gorham St., Madison, Wis. (Battery)

SAINDAS P. SHIVANI, D.C.M. Chemical Works, mailing add: 4, D.C.M. Bungalows, Rohtak Road, Delhi 6, India (Battery, Electric Insulation, and Industrial Electrolytic)

FRANKLIN C. SNOWDEN, Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia 44, Pa. (Electronics and Theoretical Electrochemistry)

K. SRINIVAS, The Mysore Electrochemical Works Ltd., Post Bag No. 1, Bangalore 2, India (Battery and Electrodeposition)

RAMASWAMIYA SUBRAMANYAM, D.C.M. Chemical Works, P.O. Box No. 1211, Delhi, India (Electrothermic and Industrial Electrolytic)

Associate Members

PATTAMADA A. CHENGAPPA, D.C.M. Chemical Works, mailing add: Flat 20, Sri Ram Bldgs., Jawaharnagar, Delhi 7, India (Industrial Electrolytic)

EDWARD F. FOLEY, JR. Columbia University, mailing add: 170 Cambridge Ave., Jersey City 7, N. J. (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

L. SUBRAMANIA PILLAI, The Mettur Chemical & Industrial Corp., Ltd., Udyogamandal P.O., Alwaye, South India (Corrosion, Industrial Electrolytic, and Theoretical Electrochemistry)

ARNOLD O. RATHJE, General Electric Co., 1099 Ivanhoe Road, Cleveland 10, Ohio (Electronics)

Student Associate Members

ATTILIO L. BISIO, Columbia University, mailing add: 25-20 21st St., Long Island City 2, N. Y. (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

RICHARD GLICKSMAN, New York University, mailing add: 492 Kosciusko St., Brooklyn 21, N. Y. (Corrosion and Theoretical Electrochemistry)

LAWRENCE R. SCHARFSTEIN, New York University, mailing add: 1466 49th St., Brooklyn, N. Y. (Corrosion)

MEETINGS OF OTHER ORGANIZATIONS

CHICAGO INTERNATIONAL TRADE FAIR, Navy Pier, Chicago, March 22–April 6.

AMERICAN SOCIETY OF MECHANICAL ENGINEERS, spring meeting, Seattle, Wash., March 24–26.

GREATER NEW YORK SAFETY COUNCIL, 22nd annual safety convention & exposition, Hotel Statler, New York City, April 1–4.

BOOK REVIEW

FLUORINE AND ITS COMPOUNDS by R. N. Haszeldine and A. G. Sharpe, Methuen's Monographs on Chemical Subjects. Published by John Wiley & Sons, Inc., New York, 1951. 153 pages, $1.75.

Prior to 1940 very few compounds of fluorine had found general use. Then, motivated by the urgency of the early phases of atomic energy development, a vigorous research effort rapidly overcame many thorny problems of fluorine technology. Today, elementary fluorine is an industrial chemical while widespread applications have been found for the remarkable properties of many of its derivatives.

Naturally, it is difficult for those not directly associated with a field of such rapid growth to keep abreast of the new developments. It was apparently with this in mind that Haszeldine and Sharpe have offered, in monograph form, a concentrated collection of the pertinent facts on "Fluorine and Its Compounds." The authors cheerfully concede that such a small book—a mere 153 pages—on such a large subject cannot of necessity be fully comprehensive. They do, however, provide a liberal sprinkling of references on the important work published before the middle of last year and include the newly introduced electrochemical synthesis of fluorocarbons.

F. H. WINSLOW

LITERATURE FROM INDUSTRY

BUFFING AND POLISHING WHEELS. Beautifully illustrated 1952 catalogue, picturing the various types of buffing and polishing wheels, is now ready for distribution. F. L. & J. C. Codman Co. P-16

ELECTRO-ANALYSIS METHODS. New 20-page manual outlining methods for the analysis of copper and lead by electroanalysis is available. The methods and extensive bibliography are a product of research at Battelle Memorial Institute. Prepared by Eberbach Corp. P-17

NOBATRONS. New catalogue giving full descriptions and up-to-the-minute ratings and specifications of the company's entire line of standard "Nobatrons" (electronically regulated d-c power sources). Sorensen & Co., Inc. P-18

TUBES, ELECTRONIC EQUIPMENT. 1952 edition of the pocket reference book describing RCA tubes, electronic components, test equipment, batteries, and miniature lamps. Includes data on characteristics interchangeability, and socket requirements of more than 450 receiving tubes, similar data on 75 dry batteries. RCA Tube Department. P-19

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

ERRATUM

In the technical article by S. T. Henderson and P. W. Ranby, in the December 1951 JOURNAL, there is a misprint in the equation on page 481, just below Fig. 4. It now reads: $I = I_0 \exp \delta\{-a(\nu - \nu_0)^2\}$. It should read: $I = I_0 \exp \{-a(\nu - \nu_0)^2\}$.

Editorial

The Electronics Division of the Society

ON THE 50th Anniversary, Divisions of the Society may well take stock of their progress. In the good old days, people wore red flannels because homes and offices were not adequately heated. Steak at one time cost only twenty cents or twenty-five cents per pound, but laborers at that time received only one dollar per day for ten hours of work. Today steak might cost one dollar per pound but the laborer receives ten dollars per day for eight hours of work. In basic terms of time and labor, steak is now only half as expensive. Even if this were not true, who would really like to give up the automobile for rides on a horsecar? Who would do without electric lights and carry an oil lamp from room to room, and live in an uninformed world without radio, vitamins, improved sanitation, or better medical care? The answer is evident. Much has been gained in 50 years. Of course, our predecessors did not know what they were missing. Improvements have not come merely because of an abundance of natural resources but they have come because men, by diligence, have learned to use those resources more effectively. Experimentally determining how to use our resources effectively is called "research."

At the beginning of the century both the electrical and the chemical industries were growing with great rapidity and this society was formed to foster developments in fields between the two. It is with pride that we can now view some of the preliminary results.

In 1902 the electric lamp was already recognized as a source of light but it was fragile, since a slight bump or vibration would break it. Its efficiency was poor and due to the low temperature of filament operation it gave much heat and what is now considered relatively poor light, largely due to the lack of radiant energy in the blue end of the visible spectrum. Ideally, a general purpose lamp should be a diffuse source of light so as not to cast deep shadows, and should have a spectral distribution at least somewhat like sunlight. It is gratifying that today, due in part at least to the members of this Division, fluorescent lamps are now many times as efficient as the old carbon filament lamps. These are relatively large sources of light and articles have more or less the same colors as in daylight. Thus, progress has been made but we will not be satisfied until a light source is found with practically 100 per cent efficiency, with both quality and quantity so improved that natural sunny conditions will prevail irrespective of time or location.

Modern trends are toward cooperation and mutual aid. At first such diverse subjects as Luminescence, Rare Metals, and Instrumentation might not seem to be closely related. A fluorescent lamp coating, however, contains rare metal compounds as in the germanate type; the lamp contains tungsten filaments which carry electron-emitting compounds. On occasion rare metals are used for gas clean-up during exhaust. Operation of the lamp involves electron emission and gaseous conduction. Photoelectric cells and meters are used for measurement of light output and fluorescent

lamps require starting switches and current-limiting auxiliary equipment. Thus it is that the fluorescent lamp is in part the problem of all three sections of the Electronics Division. From pooling of ideas and efforts within the Division, we may expect a more rapid advance in the future.

The rare metals are gradually taking their place in our daily lives. The time has already arrived when heating of buildings is being attempted by means of atomic energy from uranium. The tremendous military value of this metal is now proved fact. It is quite possible that other rare metals may be used for these purposes, but little was known about any of them when this Society was organized. Beryllium is also used in atomic energy work. Zirconium now has a definite place in the medical field and its great resistance to attack by acids will undoubtedly make it useful for many purposes. Titanium is slightly more than half as heavy as iron or steel and due to its good room-temperature strength when alloyed, it offers many structural possibilities. Germanium has, in like manner, found its way into the medical field and industrial applications in the production of transistors. Vanadium has now been produced in ductile form in the laboratory and who can tell when or how this metal may become an article of commerce? Pure, ductile, solid chromium is still a subject for research even though tremendous quantities of chromium plate are used daily by everyone. The task will not be completed until all of these rare metals are readily available and their potentialities determined.

It might be stressed that improved laboratory instruments have produced better measurements, made new products possible, and greatly reduced the time and labor of experimental work. Who would have the fortitude to attempt to exhaust large-sized furnaces or fluorescent lamps with the old hand-operated Toepler pump, or who would insist on substituting a gas-fired pot furnace for a modern high frequency oscillator when this is needed?

After fifty years on the front lines of research on electrical and rare metals problems, we have found that great new improvements are not bitter pills to swallow but always seem to make life easier and more comprehensive. Those who sigh and wish life were less complicated are simply admitting that they have failed to select from our great abundance the proper quantity they are able to digest and enjoy satisfactorily. Would anybody really want to step back half a century?

Four papers have been prepared to show how the Electronics Division has developed and to indicate the contributions it has made to the fields of Luminescence, Rare Metals, and Instrumentation. The first two of these, referring to the history of the Division and the growth of Luminescence, appear in the present issue. The other two, having to do with Rare Metals and Instrumentation, will appear next month. At that time, Former President Lawrence Addicks, one of the founders of the Society, will take the Editorial page.

These papers indicate more than just so many technical publications. They show that the Electronics Division has had officers who have worked unstintingly to promote successful meetings and maintain the interest so necessary for good programs. The authors of scientific contributions constitute a list of practically all of the great leaders in their fields.

Thanks are due to the many members who have aided in assembling these papers. J. R. Musgrave and Keith H. Butler submitted written scripts, parts of which have been included. —J. W. MARDEN

Fiftieth Anniversary

HISTORY OF THE ELECTRONICS DIVISION OF THE ELECTROCHEMICAL SOCIETY

*John W. Marden**

The birth date of this Society marks well the beginning of the tremendous developments that have taken place in the electrical field. The first two decades of the 20th Century were periods which saw the development of radio activity (discovered by Becquerel in 1896), electronic emission (Richardson 1901–1905), basic conceptions of electrical conduction, and the structure of the atom. The Electrochemical Society was organized at the beginning of this period and it could well be that our predecessors were far-seeing men who recognized the tremendous effect such discoveries were to have on scientific development.

Great industrial research laboratories were established during this period. Many of these were electrical in nature. Also, during this time the students who studied electrochemistry were trained in physical chemistry. Thus, it came about that the members of our Society became not only interested in electric furnace production of metals and chemicals or in electroplating, as measured by weight of deposit or in coulombs, but also they were interested in the fundamental processes of conduction.

Toward the latter part of the second decade, scientists were engaged in critical studies of electron emission and conduction of electricity through gases. At first, it appeared that these fields of activity were strictly those of the physicist but it soon developed that many of the problems were chemical in nature. In 1920 few three-element vacuum tubes were on the market. Everyone knows that in 1930 household radios were a necessity. In like manner, arc lamps and gaseous discharge devices were being studied in the laboratories in 1930. A few years later mercury and fluorescent lamps were common to everyone.

All of these electronic devices used thoriated, or oxide coated cathodes and the electrochemist has contributed generously to their development. The physicist studied electron emission and, with help from the electrochemist, studied gaseous discharges; it was the electrochemist who, in addition, had the problem of developing luminescent coatings. It is the electrochemist who has carried this work into the field of luminescent screens so necessary for the development of television.

The production and studies on metals, like thorium, used for electron emission became of prime importance to electrochemists. As a result, the development of the rare metals has been phenomenal. Thorium, uranium, zirconium, and titanium have been known for 100 years, but only as impure powder until intensive work was started at about the time of World War I. Since then the iodide process for zirconium and other metals, electrolytic methods for producing powder from fused baths, the calcium methods for reducing oxides, and excellent methods for reducing chlorides with magnesium have all been perfected. Rare metals were, for most chemists, names only in 1920. Today large quantities of most of these metals are being commercially produced.

As will be recognized later, members of the Society were quick to realize the importance of these new subjects; publications on selenium, for example, are to be found in our journals as early as 1903. Many individual papers of similar nature were published as time went on. The first symposium on Rare Metals was held in New York in 1923.

Since the members of this Society were called upon to contribute to this rapid development, they needed a separate division to sponsor their scientific and technical programs. A demonstration (at the Columbus Meeting in 1939) of fluorescence and phosphorescence with an ultraviolet lamp, some pieces of cloth and minerals, brought an immediate demand for sessions on luminescence and fluorescence as they applied to electrochemistry.

In order to meet this need, to offer a place where scientific discussions could be held, a division was finally formally organized within the Society called "The Electronics Division." The object of this division, as stated in the bylaws, is "to encourage education, training, research, and publication in the field of Electronics; to organize and promote formal and informal discussions in the field, and to cooperate with other sections of The Electrochemical Society." Symposia were organized on such subjects as photoelectric effects, thermionic emission, and fluorescence.

The evolution of the Electronics Division has been slow and not without some difficulties. Basic conceptions of matter have changed during the life of the Society from the point of view of elements consisting of atoms which were as indivisible as wooden balls strung on wires, to the nebulous stellar system atoms consisting mostly of voids in which electrons are always in motion. It has not been easy to show how these affect electrochemistry.

On one occasion the question of gaseous conduction was claimed not to be electrochemistry until it was pointed out that hydrogen ions were quite different chemically from hydrogen molecules and they were produced electrically. Hydrogen ions in aqueous solution, move more slowly than hydrogen ions in gaseous state. The hydrogen ion in solution, however, is burdened no doubt by many water molecules either attached to it or interfering with its progress. It has often been stated that the subject of luminescent coatings is not electrochemical, yet the coating is made by blending

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and heating processes, normally chemical, and the luminescence is produced by electrical means.

The same personnel who had problems in fluorescence were those who had problems in making rare metals or compounds thereof for photoelectric emission or thermionic emission, so that both the subjects of fluorescence and rare metals were of interest to the same scientific group. Therefore, when the Electronics Division was formally organized, it was subdivided into three groups—General Electronics, Fluorescence, and Rare Metals. Even though this division has been organized but a few short years, the term "Fluorescence" has had to be changed to "Luminescence" to cover the newer important fields of luminescent screens and phosphorescence.

At the Columbus Convention, an informal Electronics Group decided to attempt to have a symposium on fluorescence. It was felt that a symposium on this subject once every two years would be sufficient and one was held in Cleveland in 1941. In 1943 at Pittsburgh there were not only papers on photoelectric effects but also several relating to fluorescent lamps. It was agreed at the Pittsburgh meeting that the next symposium, in Philadelphia, should have more papers of fundamental importance on the subject of fluorescence and fluorescent lamps. In 1947, at Louisville, in spite of a relatively small attendance, there was sufficient interest for the division to arrange for symposia annually which could include all three fields, General Electronics, Luminescence, and the Rare Metals.

For several years a committee was active in the revision of the bylaws of the Electronics Division. These bylaws were submitted to the Board of Directors of the Society at their meeting of December 3, 1949, and were approved as submitted. Because of the diversity of interests within the Division, and in accordance with the sentiment expressed at the Columbus meeting of 1948, the new bylaws provide for the election of several vice-chairmen, each of whom will represent one of the various subjects included in the Division. After approval by the members, the bylaws took effect at the Cleveland meeting.

Thus the Society opened its doors for new subjects and made its scientific publications available to those working in the pioneer fields of the electronic arts. This forward looking policy has and can be expected to result in the further growth of the Society, not only in membership, but also in scientific leadership.

It is difficult to look back over the last fifty years with the realization of what has happened and not wonder what the future has in store. Broadly, in this period we have learned to use electricity effectively; we have, in turn, used and discarded wood as a source of energy; coal is being displaced by oil; oil by gasoline; and we have now entered an era when these will be displaced by atomic energy.

It has been pointed out that the electrochemist has contributed generously to the development of the rare metals and it is one of these metals that has now become more important than any other as a source of power, and for military purposes. No doubt the time will come when other elements will be equally important as sources of power and the electrochemist will be called upon to contribute his share in the development of this new science.

In part, even today with the use of heated wires and with the use of fluorescent coatings, we have turned night into day. Fluorescent lamps are much more efficient than filament lamps, but who could have said before 1920 that such lamps were commercially possible. Today the field of semiconductors has been studied very little. It is possible that by alternating currents, or otherwise, electrons may be moved from one energy level to another within atoms, in such manner that during their return to a stable condition light is emitted. Who can say that a far more efficient light source will not ultimately be produced. The function of the Electronics Division of The Electrochemical Society has been and will be to foster such new developments.

It should be remembered that the officers of the Division, including such names as E. G. Widell, Marlin E. Fogle, Ralph Seabury, Robert H. Schoenfeldt, and J. R. Musgrave, to mention a very few, who have done the work of assembling symposia and administering the affairs of the Division, are largely responsible for our success especially in more recent times.

This history could not be completed without mentioning the social affairs of the Society. The day has passed when the members feel duty bound to "swipe" the President's speech for the Annual Dinner, but the friendly spirit still exists wherein all are welcome and where one looks forward to meeting old friends at conventions. In spirit at least we still have Section Q.

Some of the Society's success is, of course, due to the wives who, every year, come in ever increasing numbers to enjoy the luncheons and side trips arranged for them. To the ladies we owe much for the arrangement of the social affairs, and for the great amount of work they do in preparing for our entertainment. They have kept our meetings from being "dry bone" affairs. The gracious and unselfish leadership of Mrs. Fink will never be forgotten.

To those who have spent many years in association in this Society with such scientific greats as Fink, Becket, Schlundt, C. James, Kahlenburg, etc., to name only a few, it is small wonder that this Division has flourished. Scientific researches are not like old soldiers who fade away, but they remain as foundation blocks upon which our future developments are laid.

GROWTH OF THE LUMINESCENCE SECTION

*Rudolph Nagy**

During the last fifty years the members of The Electrochemical Society played a major role in the field of lighting. When we consider that electrochemistry is the science which deals with the physical and chemical changes produced by the electric current, it becomes immediately apparent why the electrochemist interests himself in converting electrical energy into light. The numerous papers presented before the Society or published in the JOURNAL will attest to this fact. A brief survey of these papers is very revealing as to the foresight of the founders of the Society. Of special interest, is the paper of Hammer in 1903 (1) wherein many different methods of producing light were shown before the Society. As an example, Hammer demonstrated an early Edison "X-ray Lamp" which in reality was a granddaddy of our present cathode ray tube. Various phosphors such as calcium tungstate, zinc sulfide, and zinc silicate were bombarded by an electron beam to produce light. Various organic and inorganic luminescent materials were also shown which were similar, if not identical, to the ones used in many of our present-day advertising signs. Hammer also demonstrated an early Cooper-Hewitt mercury arc lamp enclosed in a screen soaked in rhodomin which was a forerunner of the present color-corrected mercury lamp using the high temperature germanate phosphor. Although the first observations of luminescence have been credited to Casciarlo, a Bologna shoemaker in 1602, synthetic phosphors at the turn of the present century remained a scientific curiosity. It was not until the development of the fluorescent lamp and the television tube that phosphors have become common place.

During the past fifty years, papers dealing with mercury and various metallic vapor arcs, suitable for lighting purposes were presented. As early as 1905, Weintraub (2) discussed the conductivity of metallic vapors for the purpose of producing light. To indicate the progress of more recent years in this field, Marden, Meister, and Beese (3) described high intensity mercury arcs operating nearly up to one thousand atmospheres and with efficiencies of over fifty lumens per watt.

Lamps producing ultraviolet radiations and their application have always been of considerable interest to the electrochemist. As an example, Baskerville (4) in 1906 had a very interesting article on the use of ultraviolet radiations in studying the fluorescence of some thirteen thousand minerals and compounds. In 1940 Knowles and Reuter (5) reported on an ultraviolet lamp used in destroying various mold, yeast, and bacteria. This is only one of the many papers of a biological nature found in the JOURNAL. In 1937 the Society conducted a symposium on Electrochemical Methods in Biology. A review of various methods was presented by the outstanding plant physiologist, Osterhout (6). Other authors discussed the use of the dropping mercury electrode, glass electrodes, and photoelectric devices as used in biology. In 1941 Klatt, *et al.* (7) had an interesting paper on the use of the dropping electrode in the diagnosis of cancer.

Various instruments and their uses have always interested the electrochemist, as is evidenced by the numerous papers on instrumentation. As an example, Zworykin (8) was invited in 1941 to speak before the Society on the electron microscope. This tool has proved to be useful in many electrochemical processes. One of these is reported by Mrgudich and Clock (9, 10) on x-ray and electron microscope studies of carbon black. This instrument has also been extensively used in the study of various phosphors. The x-ray diffraction apparatus has been used on such diverse materials as phosphors by Fonda and Froelich (11), silicon monoxide films by Braumann (12), and rectifying selenium films by Clark and Roach (13). It has in reality become a standard tool in most laboratories. Other instruments such as automatic temperature controls described by Fogle (14) or *p*H controls described by Greer and Chalpin (15) which were nonexistent at the turn of the century have become commonplace in industry today. Various types of photocells as described by Fink, *et al.* (16, 17) and later by Rentschler and Henry (18) have become useful tools. The electrochemist has contributed to the knowledge of instrumentation and has taken advantage of new tools developed in other fields.

Throughout the history of the Society, various theoretical aspects of gaseous conduction were discussed. As early as 1903, Parsons (19) described electron conduction in vacuum tubes. In 1923, Lind (20) directed a symposium on the electrochemistry of gaseous conduction. A total of sixteen papers was presented by such outstanding scientists as F. H. Newman, S. Dushman, K. T. Compton, and many others. In 1936, Darrow (21) presented an informative lecture on electricity in gases. Gaseous conduction in lamps was also discussed by Buttolph (22) and van der Werfhorst (23). Papers of this nature were setting the stage for the fluorescent lamp which appeared on the scene in 1938.

However, before the world was ready for the fluorescent lamp, considerable progress was reported to the Society on incandescent lamp sources. As early as 1905, Roeber (24) demonstrated the first tantalum, osmium, and graphitized carbon lamps to be shown in this country. Bancroft (25) in 1908 discussed the various aspects of the electrochemistry of light and Ives (26) in 1915 presented a paper on the conception of an ideal light. Most of the early lighting engineers were mainly concerned with the development of filaments capable of operating at high temperatures.

It was not until 1939 that Marden (27) demonstrated before the Society various fluorescent materials and talked on the new fluorescent lamp, pointing out that the art of converting electrical energy into light had passed another milestone. Before the conclusion of this meeting various members of the Electronics Division organized a Luminescence subsection which was to present periodic symposia on luminescence.

The first Society Luminescence Symposium was held in 1945, at which time eight papers on phosphors and fluorescent lamps were presented. The symposium was a success. Thayer (28) gave an informative paper on the quantum efficiency of fluorescent lamps. His calculations indicated that the fluorescent lamp with zinc beryllium phosphor has a quantum efficiency of ninety per cent. Kenty and Cooper

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FIG. 1. Inspection of glass tubes used in fluorescent lamps

(29) showed the effect of various common gas impurities on the output and operation of the fluorescent lamp. Such gases as oxygen, carbon dioxide, and water vapor react with mercury to give a black mercury oxide that greatly decreases light output.

At the next luminescence meeting which was held in Louisville in 1947, Froelich (30) presented a paper on a new ultraviolet phosphor, making it possible for the first time to make an efficient fluorescent sunlamp. Butler (31) also presented one of a series of papers on barium silicate phosphors, some of which proved useful as "black-light" phosphors. Of considerable interest was the paper of Bramley (32) on aluminum-backed phosphor screens in cathode ray tubes. These tubes can be operated at a higher voltage, have a higher output, and the aluminum reduces the tendency of phosphor deterioration. The postwar years stimulated considerable demand for fluorescent lamps and television tubes. A tremendous amount of energy was expended in research on new and better phosphors and their application. Most of the scientific papers that have resulted from such research, have been presented at the Luminescence Symposia. Their number has increased phenomenally.

In 1948 Froelich (33) reported on a new calcium silicate phosphor which at present is used in many color corrected fluorescent lamps. Smith (34) showed the importance of atmosphere on the firing of zinc sulfide phosphors. This paper and those of Kroeger (35) show the sulfide phosphors are much more complex in their constitution than was realized by Lenard at the turn of the century. This is also exemplified by the paper of Ward (36) who reported on the doubly activated alkaline earth sulfides. The energy stored by the phosphor as a result of ultraviolet excitation is released upon infrared excitation. The emission spectrum is governed by one of the activators while the infrared excitation spectrum is governed by the other impurity.

In 1949 a total of twenty-six papers dealing with all phases of luminescence was published in the JOURNAL. It would be beyond the scope of this brief summary to comment on all of the various papers. This was very ably done by Fonda (37) in his review of articles on luminescence for 1949. Of special interest was the paper of Jenkins, *et al.* (38), on alkaline earth halophosphates. These phosphors have completely replaced the zinc beryllium silicates used in fluorescent lamps up to this date. A number of papers on the mechanism of luminescence have also been presented. Both Kroeger (39) and Smith (40) reported that a part of the flux used in the formation of sulfide phosphors may become an essential ingredient of the phosphor. Garlich (41) working on the thermoluminescence of phosphors was able to correlate the effect of constitution and activator upon the trap depths of zinc sulfide phosphors. The advancement in the art of cathode ray tube manufacture can best be exemplified by the article of Sedowsky (42). He described all of the then available methods of screen application. Two years later, eleven papers dealing with various phases of this subject were discussed before the newly formed Screen Application section. This is a very good example of the phenomenal growth of certain phases of science and the ability of the Society to meet the needs of its members.

A summary of luminescence for the year 1950 was also compiled by Fonda (43). Of the many new phosphors reported, $CaO \cdot MgO \cdot 2SiO_2$:Ti discovered by Smith (44) is of interest because of its high efficiency under cathode ray bombardment and since it contains titanium as an activator. Most of the silicates in the past have been activated with manganese. In calcium zinc silicate activated with thallium, Nagy, *et al.* (45) found the addition of zinc to shift the emission spectrum to the shorter wavelength. At the Washington meeting in

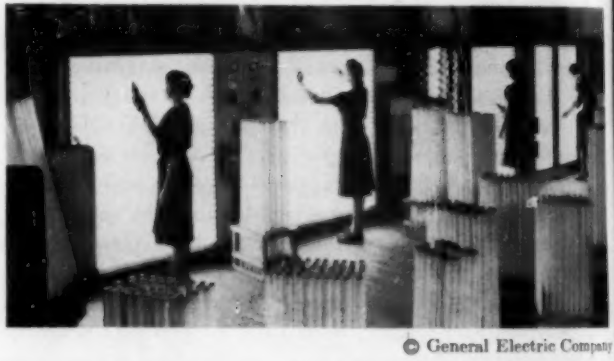

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FIG. 2. Factory seasoning of glass tubes

1951, a large number of interesting new phosphors were described. Of note was barium titanium phosphate of Henderson and Ranby (46) which contained thirty mole per cent titanium oxide. This phosphor has an output and spectral distribution very similar to magnesium tungstate. Prener (47) showed that an efficient zinc sulfide phosphor can be made using arsenic as an activator. Froelich, *et al.* (48) spoke on a red emitting calcium phosphate activated with cerium and manganese. He also discovered that a small per cent of potassium or sodium greatly increased the stability and temperature dependence of this phosphor. Another red phosphor, zinc phosphate activated with manganese, was reported by Smith (49). X-ray diffraction patterns showed this phosphor to exist in different forms depending upon the temperature of heating and manganese concentration. Payne, *et al.* (50) showed the direct excitation of phosphors by electric fields. This principle first demonstrated by Destriau in 1937 is very intriguing both from the theoretical as well as practical standpoint. If more efficient phosphors can be found, this may prove to be our mode of lighting in the future.

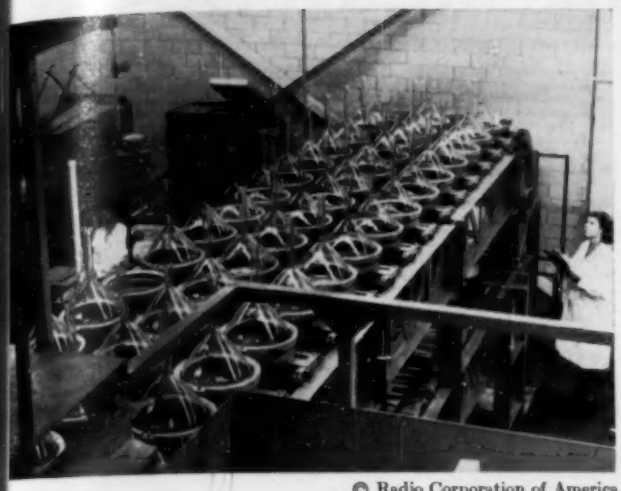

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FIG. 3. Putting "picture face" on television cathode ray tubes by a settling process.

This brief survey depicting the role that The Electrochemical Society played in the advancement of the science of lighting and associated arts for the past fifty years does not claim to be a review of literature of the subject. Rather it was written to show the phenomenal progress made in this field by highlighting a few of the contributions made by its members. In addition to those mentioned, there are many papers of importance throughout the JOURNAL and another writer could have easily made another list of names of authors as imposing as the one presented. The phenomenal growth during the past few years clearly indicates the trend of the increasing stature of the Society. Our knowledge, especially of phosphors, is still in its infancy. There is a great deal to be learned regarding the mechanisms of luminescence. We are in need of better phosphors for fluorescent lamps, television tubes, and more efficient high temperature and ultraviolet emitting phosphors. It is predicted that many of these new discoveries will be reported before the Electronics Division and thus The Electrochemical Society will play a major role in this field.

In the fluorescent lamp industry, glass tubes are coated by flushing the tube with a suspension of fluorescent material in an organic binder and drying and baking. Inspection of these tubes is shown in Fig. 1. Tungsten coil filaments coated with electron emitting compounds are sealed into each end and the lamps are exhausted while hot. Fig. 2 shows the factory seasoning of tubes prior to packing for shipment.

Fig. 3 and 4 pictorially show some of the processes employed in producing television tubes. Luminescent materials are now produced synthetically in relatively large quantities. The "picture face" is put on television cathode ray tubes by a settling process. This must be done under conditions free of vibration (Fig. 3). A conductive coating is also put on the inside of the tube to trap secondary electrons that bounce off the fluorescent screen (Fig. 4). Following this, the emitting cathode and control electrodes are sealed. As with fluorescent lamps, television tubes are carefully seasoned and tested prior to packing and shipping. Fig. 5 indicates some of the research necessary for such development. Here the spectral distribution of light emitted by phosphors is being measured.

REFERENCES

(References listed below appear in the Journal or Transactions of The Electrochemical Society)

1. WILLIAM J. HAMMER, "Radium and other Radioactive Substances with a Consideration of Phosphorescent and Fluorescent Substances. The Properties and Applications of Selenium and the Treatment of Disease by the Ultraviolet Light," **3,** appendix, (1903).
2. E. WEINTRAUB, "The Mercury Arc," **7,** 273, (1905).
3. G. MEISTER, J. W. MARDEN, and N. C. BEESE, "The Characteristics of High Intensity Mercury Arc Lamps," **69,** 389, (1936).
4. CHARLES BASKERVILLE, "Ultra-Violet Light in the Laboratory and in Practice," **10,** 123, (1906).
5. D. D. KNOWLES AND E. REUTER, "The Sterilamp. Its Electrical and Radiation Characteristics," **78,** 21, (1940).
6. W. J. V. OSTERHOUT, "Electrochemical Methods in the Study of Plant Cells," **71,** 93, (1937).
7. T. KLATT, H. P. RUSCH, A. DIRKSEN, AND V. W. MELOCHE, "Diagnosis of Cancer by Means of the Dropping Mercury Electrode," **79,** 413, (1941).
8. VLADIMIR K. ZWORYKIN, "The Electron Microscope," **80,** 14, (1941).
9. J. N. MRGUDICH, "X-Ray Studies of Storage Battery Pastes," **81,** 165, (1942).
10. J. N. MRGUDICH AND R. C. CLOCK, "X-Ray and Electron Microscope Evaluation of Carbon Blacks," **86,** 351, (1944).
11. G. R. FONDA AND H. C. FROELICH, "The Structure of Calcium Silicate Phosphors," **93,** 114, (1948).

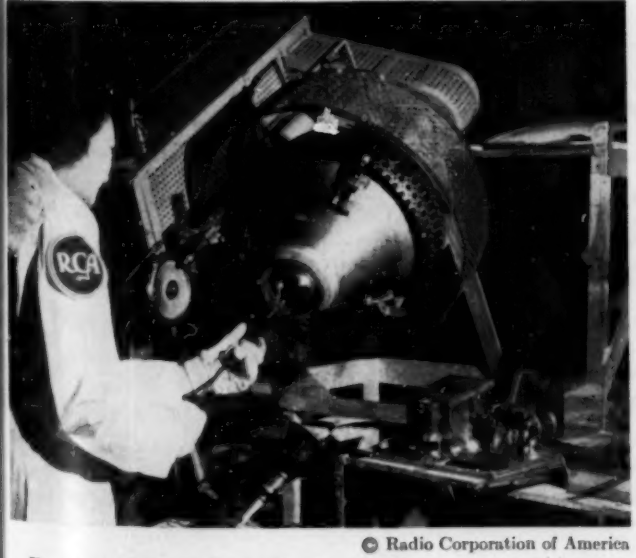

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FIG. 4. A conductive coating being put on the inside of the television tube to trap secondary electrons.

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FIG. 5. Measuring spectral distribution of light emitted by phosphors in research lab.

12. H. N. Baumann, Jr., "The X-Ray Diffraction Examination of Material having the Composition SiO," **80**, 95, (1941).
13. G. L. Clark and P. G. Roach, "An X-Ray Study of the Structure of Rectifying Selenium Films," **79**, 355, (1941).
14. M. E. Fogle, "Temperature Measurement and Control with Solid Photoelectric Cells," **83**, 77, (1943).
15. W. N. Greer and A. L. Chaplin, "Some Factors Affecting Automatic pH Control," **83**, 67, (1943).
16. C. G. Fink and E. Adler, "Semi-Conductor Photocells and Rectifiers," **79**, 377, (1941).
17. C. G. Fink and J. S. Mackay, "Photoelectric Cells Sensitive to Long Wave Length Radiation. The Bismuth Sulfide Cell," **77**, 299, (1940).
18. H. C. Rentschler and D. E. Henry, "Lowering of the Photoelectric Work Function of Zirconium, Titanium, Thorium, and Similar Metals by Dissolved Gases," **87**, 289, (1945).
19. L. A. Parsons, "Ions and Electrons," **3**, 265, (1903).
20. S. C. Lind, "The Electrochemistry of Gases," **44**, 63, (1923).
21. K. K. Darrow, "Electricity in Gases," **69**, 67, (1936).
22. L. J. Buttolph, "The Development of Gaseous Conduction Lamps," **65**, 143, (1934).
23. G. B. van der Werfhorst, "The Development of Gaseous Discharge Lamps in Europe," **65**, 157, (1934).
24. E. F. Roeber, "Thermodynamics of the Electric Incandescent Lamp," **8**, 243, (1905).
25. W. D. Bancroft, "The Electrochemistry of Light," **13**, 243, (1908).
26. H. E. Ives, "An Illuminating Engineer's Conception of an Ideal Light," **27**, 419, (1915).
27. J. W. Marden, "The New Fluorescent Lamp," **75**, 64, (1939).
28. R. N. Thayer, "Some Physical Properties of Fluorescent Lamp Coatings," **87**, 413, (1945).
29. Carl Kenty and J. R. Cooper, "A Study of the Effects of Gas Impurities in Fluorescent Lamps," **87**, 397, (1945).
30. H. C. Froelich, "New Ultraviolet Phosphors," **91**, 241, (1947).
31. K. H. Butler, "Barium Silicate Phosphors," **91**, 265, (1947).
32. Arthur Bramley, "Aluminum Backed Phosphor Scr in Cathode Ray Tubes," **91**, 279, (1947).
33. H. C. Froelich, "Manganese Activated Calcium Silic Phosphors," **93**, 101, (1948).
34. A. L. Smith, "Influence of Atmosphere Firing on Cathodoluminescence of Zinc Sulfide: Silver Type Ph phors," **93**, 324, (1948).
35. F. A. Kroeger and J. E. Hellingman, "The Blue L minescence of Zinc Sulfide," **93**, 156, (1948).
36. Roland Ward, "Infrared-Sensitive Phosphors of the Alk line Earth Sulfides and Selenides," **93**, 171, (1948).
37. G. R. Fonda, "Review of Articles on Luminescence 1949," **97**, 3C, (1950).
38. H. G. Jenkins, A. H. McKeag, and P. W. Ranby, "Alkali Earth Halophosphates and Related Phosphors," **96**, (1949).
39. F. A. Kroeger and J. E. Hellingman, "Chemical Pro of the Presence of Chlorine in Blue Fluorescent Zi Sulfide," **95**, 68, (1949).
40. A. L. Smith, "Influence of Fluxes on the Cathodolumin cence of Zinc Sulfide Phosphors," **96**, 75, (1949).
41. G. F. J. Garlick and D. E. Mason, "Electron Traps a Infrared Stimulation of Phosphors," **96**, 90, (1949).
42. M. Sadowsky, "Preparation of Luminescent Screens," 112, (1949).
43. G. R. Fonda, "Review of Articles on Luminescence 1950," **98**, 35C, (1951).
44. A. L. Smith, "Some New Complex Silicate Phosphors Co taining Calcium, Magnesium, and Beryllium," **96**, (1949).
45. R. Nagy, R. W. Wollentin, C. K. Lui, "Ultraviolet Emi ting Phosphor," **97**, 29, (1950).
46. S. T. Henderson and P. W. Ranby, "Barium Titaniu Phosphate: A New Phosphor," **98**, 479, (1951).
47. J. S. Prener, "An Arsenic-Activated Zinc Sulfide Pho phor," **98**, 406, (1951).
48. H. C. Froelich and J. M. Margolis, "Calcium Phosphat Phosphor Activated with Cerium and Manganese," 400, (1951).
49. A. L. Smith, "Luminescence of Three Forms of Zinc Ortho phosphate: Mn," **98**, 363, (1951).
50. E. C. Payne, E. L. Mager, and D. W. Jerome, "Direc Excitation of Phosphors by Electric Fields," Abstract 49, Washington Meeting, (1951).

Current Affairs

Plans Now Complete for Philadelphia Meeting

All arrangements for the well-planned Fiftieth Anniversary Meeting of the Society in Philadelphia, May 4 through 8, have been completed, according to latest reports from General Chairman Hiram S. Lukens. The members of the various Convention Committees express satisfaction with the program, and it is expected that both the social and technical schedule will prove gratifying to the large attendance that is anticipated.

Headquarters for the meeting is the Benjamin Franklin Hotel, Ninth and Chestnut Streets. Registration will start on Sunday evening, from 8:30 to 10:00 P.M., and will continue on Monday through Thursday. A brief schedule of the Luncheons, Ladies' Program, etc. appears below, followed by the complete technical program which will include about 120 papers. For more complete details of convention activities, see the February and March JOURNALS, and consult your Program Booklet.

Luncheons

The following divisional luncheons have been scheduled: Theoretical Division, Monday, May 5th; Electronics Division, Wednesday, May 7th; Electrothermic Division, Thursday, May 8th.

The General Luncheon, to which the ladies are invited, will be held on Tuesday, May 6th. The speaker will be Dr. William Page Harbeson, John Welsh Centennial Professor of History and English Literature, of the University of Pennsylvania.

Ladies' Program

Monday May 5th, 11:30 A.M. Reception and "Kaffee Klatsch" when arrangements will be made for trips to points of historic interest, shopping centers, etc.

Monday, May 5th, 8:00 P.M. Canasta and Bridge Party.

Tuesday, May 6th, 1:00 P.M. General Luncheon.

HIRAM S. LUKENS

Tuesday, May 6th, 7:00 P.M. President's Reception and Annual Banquet.

Wednesday, May 7th, 11:00 A.M. Leave by bus for luncheon at Huntington Valley Country Club. Talk and demonstration of "Flower Arrangements" by Mrs. Blanche Scarlett Phelps. Trip to Bryn Athyn Cathedral.

Wednesday, May 7th, 7:00 P.M. Buffet Supper and Entertainment.

Plant Trips

On Wednesday, May 7th, there will be an inspection trip to the new long-distance dialing installation of the Bell Telephone Company. The visitors will be shown how calls are routed automatically throughout the Bell System.

As previously announced, Security Regulations have made it impossible to schedule other plant trips. It may be possible, however, to arrange trips for individuals or small groups to factories in which they might be interested. Plant Trip Committee Chairman, Milton P. Barba, of Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia 44, will undertake to make the necessary arrangements if notice is given him well in advance of the meeting.

Technical Program

Monday, May 5, 1952

9:00 A.M.—Formal Opening of the Fiftieth Anniversary Convention with Introduction by General Chairman Hiram S. Lukens and response by President R. M. Hunter.

Electric Insulation

Tuesday, May 6, 1952

The Chemical and Physical Properties of Dielectrics

John J. Chapman presiding

9:00 A.M.—"A Revised Theory of Dielectrics" by Franklin H. Branin, Jr., University of California, Los Alamos Scientific Laboratory, Los Alamos, N. Mex.

9:45 A.M.—"The Electrical Properties of Paper Made From Ceramic Fibers" by Thomas D. Callinan and R. T. Lucas, Naval Research Laboratory, Washington, D. C.

10:30 A.M.—"Oxidative Degradation of Polyvinylformal, II. The Gas Phase" by Harold C. Beachell and Leonard Cutler, University of Delaware, Department of Chemistry, Newark, Del.

11:15 A.M.—"A Study of the Properties of the Residual Water in Highly Desiccated Amorphous Solids" by Walter A. Patrick, Department of Chemistry, The Johns Hopkins University, Baltimore, Md.

Electric Insulation (cont'd.)

Wire and Cable Insulants

J. Robert Bukey presiding

2:00 P.M.—"The Manufacture and Properties of Cable Paper" by De Loss Kahl, Jr., Merrimac Paper Company, New York, N. Y.

2:45 P.M.—"Film Formation on Metals

in Hydrocarbons" by A. Gemant, The Detroit Edison Company, Detroit, Mich.

3:30 P.M.—"The Electrical Properties and Applications of Fibrous Glass" by Kenneth E. Lydic, Electrical Products Development Laboratory, Owens-Corning Fiberglas Corporation, Ashton, R. I.

4:15 P.M.—"The Manufacture and Processing of Mica Paper for Use in Electric Insulation" by R. L. Griffeth and E. R. Younglove, Mica Insulator Company, Schenectady, N. Y.

Wednesday, May 7, 1952

Electric Insulation (cont'd.)

The Manufacture of Plastics for the Electrical Insulation Trade

J. Robert Bukey presiding

9:00 A.M.—"The Part Some Plastics Play in the Electrical Industry" by F. J. MacRae, Plastics Division, Dow Chemical Company, Midland, Mich.

9:30 A.M.—"The Role of Fillers in the Manufacture of Vinyl Insulation" by E. W. Schwartz, Southern Clays, Inc., New York, N. Y.

10:00 A.M.—"The Role of Plasticizer in the Manufacture of Vinyl Insulation" by George R. Buchanan, Monsanto Chemical Company, Springfield, Mass.

10:30 A.M.—"Dynamic Electrical and Mechanical Behavior of Polymeric Systems" by Edwin R. Fitzgerald, University of Wisconsin, Madison Wis.

11:15 A.M.—"Manufacture and Uses of Silicone Fibers" by V. A. Wente, Naval Research Laboratory, Washington, D. C.

Electric Insulation (cont'd.)

The Electrical Properties of Plastics

Leon L. Deer presiding

2:00 P.M.—"Effect of Chemical Structure on the Electrical Properties of Synthetic, Organic, Solid Insulating Materials" by Henry M. Richardson, DeBell and Richardson, Inc., Springfield, Mass.

2:45 P.M.—"A New Class of Synthetic Fabrics for Insulating Uses" by Arthur C. Wrotnowski, American Felt Company, Glenville, Conn.

3:30 P.M.—"The Testing of Molded Dielectrics" by A. L. Coats and Carl Pomeroy, Scintilla Magneto Division, Bendix Aviation Corporation, Sidney, N. Y.

4:15 P.M.—"The Use of the Epoxy Type Resins as a Dielectric" by Paul L. Hedrick, Minnesota Mining and Manufacturing Company, St. Paul, Minn.

Thursday, May 8, 1952

Electric Insulation (cont'd.)

The Evaluation of Dielectrics

Leon L. Deer presiding

9:00 A.M.—"Apparatus for Developing Electric Breakdown Voltages at High Frequencies" by Louis J. Frisco, Institute for Co-operative Research, The Johns Hopkins University, Baltimore, Md.

9:30 A.M.—"The Electric Strength of Sulfur Hexafluoride at Radio Frequencies" by John W. Gibson and C. Frank Miller, Department of Electrical Engineering, The Johns Hopkins University, Baltimore, Md.

10:00 A.M.—"Tracking of Plastics Under Low Power Electrical Discharges" by Murray Olyphant, Princeton University, Princeton, N. J.

10:30 A.M.—"The Shrinkage of Molded Plastics" by Harry M. Neben, American Phenolic Corporation, Chicago, Ill.

11:15 A.M.—"The Effect of Humidity Upon the Insulation Resistance of Alkyd Molding Compounds" by M. H. Bigelow and P. E. Nowicki, Plaskon Division, Libby Owens Ford Company, Toledo, Ohio.

Electric Insulation (cont'd.)

The Manufacture and Properties of Electrical Condensers and Impregnants

Ralph A. Ruscetta presiding

2:00 P.M.—"Internal Junction Capacitance Standards" by John A. Connor, Leeds & Northrup, Philadelphia, Pa.

2:45 P.M.—"Fluorinated Liquids for Dielectric Applications" by N. M. Bashara, Central Research Department, Minnesota Mining and Manufacturing Company, St. Paul, Minn.

3:30 P.M.—"Distribution of Conductivity within the Dielectric Film on Aluminum" by J. E. Lilienfeld and Charles Miller, Power Condenser and Electronics Corporation, Washington, D. C.

4:15 P.M.—"Tantalum Capacitors" by L. W. Foster, Capacitor Department, General Electric Company, Hudson Falls, N. Y.

Electronics—Instrumentation

Wednesday, May 7, 1952

R. H. Cherry presiding

9:00 A.M.—Introductory Remarks by R. H. Cherry,

9:05 A.M.—"An Automatic Titrator Using Electrolytically Generated Reagents" by W. N. Carson, Jr., General Electric Company, Nucleonics Department, Hanford Works, Richland, Wash.

9:35 A.M.—"Coulometric Acidimetry and Alkalimetry" by Donald D. DeFord, Donald T. Hooker, James M. Thoburn, and James N. Pitts, Northwestern University, Evanston, Ill.

10:05 A.M.—"An Electrolysis Instrument for Continuously Recording the Concentration of Dilute Chlorine Water" by Edgar L. Eckfeldt, William E. Proctor, and George A. Perley, Leeds & Northrup Company, Philadelphia, Pa.

10:35 A.M.—"High Frequency Titration and Dielectric Measurement with a New Instrument" by Robert R. Austin, Beckman Instruments, Inc., South Pasadena, Calif.

11:05 A.M.—"Stabilized *p*H Indicator" by W. R. Clark and G. A. Perley, Leeds & Northrup Company, Philadelphia, Pa.

11:35 A.M.—"Electroadsorption Analysis by Transitory Time Measurements" by Lucien Gierst and André Juliard, University of Brussels, Brussels, Belgium.

12:05 P.M.—"The Operating Characteristics of the Leeds & Northrup Type E Electrochemograph" by C. E. Bricker and W. C. Cooper, Department of Chemistry, Princeton University, Princeton, N. J.

Electronics—Luminescence

Monday, May 5, 1952

Roland Ward presiding

9:15 A.M.—Introductory Remarks.

9:20 A.M.—Keynote Address, "The Nature of Fluorescent Centers and Traps in Zinc Sulfide Phosphors" by H. A. Klasens, Philips Research Laboratories, Eindhoven, The Netherlands.

10:00 A.M.—"Multiple Emission Bands in Zinc-Cadmium Sulfide Phosphors" by G. R. Fonda, E. B. Fehr, A. I. Friedman, and F. J. Studer, General Electric Company, Schenectady, N. Y.

10:25 A.M.—"Review of Trapping in Phosphors" by R. H. Bube, Radio Corporation of America, RCA Laboratories Division, Princeton, N. J.

10:55 A.M.—"Determination of Electron-Trap Distributions from Phosphorescence Decay Measurements" by G. M. Nazarian, Physics Labora-

tories, Sylvania Electric Products Inc., Kew Gardens, N. Y.

11:25 A.M.—"Some Properties of Zinc Sulfide Activated with Copper and Cobalt" by W. Hoogenstraaten and H. A. Klasens, Philips Research Laboratories, Eindhoven, The Netherlands.

11:50 A.M.—"The Chemistry of Traps in Zinc Sulfide Phosphors" by W. Hoogenstraaten, Philips Research Laboratories, Eindhoven, The Netherlands.

Electronics—Luminescence (cont'd.)

Horace H. Homer presiding

2:00 P.M.—"A 2537 Å Reflectometer for Fluorescent Lamp Phosphors" by John O. Aicher, Nela Lamp Works, General Electric Company, Cleveland, Ohio.

2:20 P.M. — "Cathodoluminescence Characteristics of Some Barium-Zinc-Silicate Phosphors with Manganese Activator" by Simon Larach, Radio Corporation of America, RCA Laboratories Division, Princeton, N. J.

2:45 P.M.—"The Optical Properties of Phosphors and Their Quantum Efficiencies" by Shannon Jones and G. R. Fonda, General Electric Company, Schenectady, N. Y.

3:10 P.M.—"Intrinsic Efficiencies of Phosphors under Cathode Ray Excitation" and "New Phosphors for Flying Spot Cathode Ray Tubes" by A. Bril and H. A. Klasens, Philips Research Laboratories, Eindhoven, The Netherlands.

3:45 P.M.—"Alkaline Earth Phosphate Phosphors" by Keith H. Butler, Sylvania Electric Products Inc., Salem, Mass.

4:10 P.M.—"Zinc Phosphate Silicates Activated by Manganese" by P. Zalm, Philips Research Laboratories, Eindhoven, The Netherlands.

4:35 P.M.—"The Dependence of Luminescent Efficiency on Activator Concentration," "The Effect of Concentration of Activator, of Temperature and of Flux on the Excitation and Emission of CaO:B. Phosphors," and "The Emission and Excitation Spectra of CaO Phosphors with Eleven Different Activators" by J. Ewles and N. Lee, Department of Physics, The University of Leeds, England.

Tuesday, May 6, 1952

Electronics—Luminescence (cont'd.)

Arthur L. Smith presiding

9:00 A.M.—"Electroluminescent Zinc Sulfide, I. Electrical Measurements" by C. W. Jerome and W. C. Gungle, Sylvania Electric Products Inc., Salem, Mass.

9:20 A.M.—"Electroluminescent Zinc Sulfide, II. Optical Measurements" by J. F. Waymouth and C. W. Jerome, Sylvania Electric Products Inc., Salem, Mass.

9:40 A.M.—"Electroluminescent Zinc Sulfide, III. Interpretation of Experimental Results" by J. F. Waymouth, Sylvania Electric Products Inc., Salem, Mass.

10:05 A.M.—"Electroluminescence of Phosphors in Vacuo" by Luke Thorington, Research Department, Westinghouse Lamp Division, Bloomfield, N. J.

10:30 A.M.—"The Effect of Double Activation on the Dielectric Constant of Strontium Sulfide Phosphors" by W. Kiszenick and J. J. Dropkin, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

10:55 A.M.—"The Dielectric Aspects of Electroluminescence" by Laurence Burns, Sylvania Electric Products Inc., Salem, Mass.

11:20 A.M.—"Energy Transfer in Sensitized Phosphors" by Th. P. J. Botden, Philips Research Laboratories, Eindhoven, The Netherlands.

2:00–5:00 P.M.—Round-Table Discussion led by James H. Schulman.

Electronics—Rare Metals

Wednesday, May 7, 1952

The Iodide Process for Metals

A. U. Seybolt presiding

9:00 A.M.—Introductory Remarks by D. M. Wroughton

9:10 A.M.—Keynote Address, "Our 50 Years" by John W. Marden, Westinghouse Lamp Company, Bloomfield, N. J.

9:30 A.M.—"Preparation of 'Mischmetall' by Thermal Reduction" by C. Decroly, J. Van Impe, and D. Tytgat, Department of Metallurgy and Electrochemistry, University of Brussels, Brussels, Belgium.

10:00 A.M.—"The Preparation and Properties of Iodide Vanadium" by Julian W. Nash, Richard E. Durtschi, I. E. Campbell, and R. I. Jaffee, Battelle Memorial Institute, Columbus, Ohio.

10:20 A.M.—"The Properties of High-Purity Iodide Chromium" by Harry Goodwin, Robert Gilbert, and C. M. Schwartz, Battelle Memorial Institute, Columbus, Ohio.

10:40 A.M.—"A Systematic Study of the Deposition Process for Iodide Zirconium" by Z. M. Shapiro, Westinghouse Electric Corporation, Atomic Power Division, Pittsburgh, Pa.

11:00 A.M.—"The Hot-Wire Process for Zirconium" by Robert B. Holden and Bernard Kopelman, Sylvania Electric Products Inc., Bayside, N. Y.

11:20 A.M.—"Factors Influencing the Rate of Deposition of Metals in the Van Arkel-de Boer Process" by C. E. Dryden, J. M. Blocher, Jr., and I. E. Campbell, Battelle Memorial Institute, Columbus, Ohio.

11:45 A.M.—"The Preparation of High-Purity Chromium from Chromous Iodide" by Robert Gilbert, Harry Goodwin, John M. Blocher, Jr., and I. E. Campbell, Battelle Memorial Institute, Columbus, Ohio.

12:00 M.—Discussion on the Iodide Process.

Electronics—Rare Metals (Cont'd)

The Uncommon Metals

D. M. Wroughton presiding

2:00 P.M.—"Zirconium Metal Powder" by Holger C. Andersen and Lawrence H. Belz, Research and Development Laboratory, Foote Mineral Company, Berwyn, Pa.

2:30 P.M.—"The Recovery, Production, and Potential Uses of Gallium" by A. Paul Thompson and H. R. Harner, The Eagle-Picher Research Laboratories, Joplin, Mo.

3:00 P.M.—"Preparation of Yttrium and Some Heavy Rare Earth Metals" by F. H. Spedding and A. H. Daane, Institute for Atomic Research, Iowa State College, Ames, Iowa.

3:30 P.M.—"Effect of Germanium on the Transformation of White to Gray Tin at Comparatively Low Temperature" by R. R. Rogers and J. F. Fydell, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

4:00 P.M.—"Methods of Characterizing an Etched Surface" by I. Goldman, Physics Laboratories, Sylvania Electric Products Inc., Bayside, N. Y.

Electronics—Screen Application

Wednesday, May 7, 1952

A. E. Hardy presiding

(Harrison Laboratory, University of Pennsylvania)

To attend Wednesday afternoon session on Screen Application, take car 13 or 42 west-bound on Walnut Street at Ninth to Harrison Laboratory at 34th

and Spruce Streets. Session will be held in the Lecture Theatre. Returning, take car 42 east-bound on Spruce Street to hotel at Ninth and Chestnut Streets. This trip requires 15 to 20 minutes.

2:00 P.M.—Introductory Remarks.

2:05 P.M.—"Preliminary Investigation of the Cause and Reduction of Cross-Burning on 20CP4 Cathode Ray Tubes by R. Granacki, Sarkes Tarzian, Inc., Chicago, Ill.

2:35 P.M.—"Evaluation of Commercial Interior Coatings for Cathode Ray Tubes" by D. T. Palumbo, Sylvania Electric Products Inc., Flushing, N. Y.

3:05 P.M.—"Organic Impurities in Deionized Water and Their Elimination" by R. B. Snyder, Rauland Corporation, Chicago, Ill.

3:35 P.M.—"Streaming Potential Measurements and the Adhesion of Phosphors" by J. F. Hazel and George L. Schnable, University of Pennsylvania, Philadelphia, Pa.

4:20 P.M.—Demonstration of Streaming Potential Equipment by J. F. Hazel, University of Pennsylvania, Philadelphia, Pa.

Joint Session

Electrothermics—Rare Metals

Thursday, May 8, 1952

General Electrothermics

S. J. Sindeband presiding

9:00 A.M.—"The Manufacture of Boron" by G. H. Fetterley, Norton Company, Niagara Falls, Canada.

9:30 A.M.—"Uranium Sesquicarbide" by M. W. Mallett, A. F. Gerds, and D. A. Vaughan, Battelle Memorial Institute, Columbus, Ohio.

10:00 A.M.—"The Uranium-Carbon System" by M. W. Mallett, A. F. Gerds, and H. R. Nelson, Battelle Memorial Institute, Columbus, Ohio.

10:30 A.M.—"Radiation Pyrometry" by W. T. Gray, Leeds & Northrup Company, Philadelphia 44, Pa.

11:00 A.M.—"A Technique for Eliminating Crucibles in Heating and Melting of Metals" by D. M. Wroughton and E. C. Okress, Westinghouse Electric Corporation, Bloomfield, N. J., and P. H. Brace, G. Comenetz, and J. C. R. Kelly, Westinghouse Electric Corporation, East Pittsburgh, Pa.

Joint Session

Round-Table Discussion

Methods of Refractory Metal Melting

R. L. Hadley, Chairman
and R. M. Parke, Moderator

2:00–5:30 P.M.—The session will be introduced by ten-minute talks by participants representing groups engaged in research or production involving refractory metals. Talks will cover work in areas of interest to the individual, his view of the status of development of the refractory metal field, and analysis of problems requiring solution. An open discussion on the various subjects will follow.

Theoretical Electrochemistry

Monday, May 5, 1952

Polarization

Walter J. Hamer presiding

9:15 A.M.—Introductory Remarks.

9:20 A.M.—"The Measurement of Capacity and Surface Area of Platinum Electrodes" by W. D. Robertson, Hammond Metallurgical Laboratory, Yale University, New Haven, Conn.

9:50 A.M.—"Theory of Pseudo-Capacity and the Faradaic Admittance" by David C. Grahame, Department of Chemistry, Amherst College, Amherst, Mass.

10:25 A.M.—"Non-Uniform Electrode Surfaces and Changes in Overvoltage with Time" by W. Busing, Sterling Chemistry Laboratory, Yale University, New Haven, Conn., and W. Kauzmann, Frick Chemical Laboratory, Princeton University, Princeton, N. J.

10:55 A.M.—"Polarization Phenomena at Twofold Electrodes" by Erich Lange, Laboratory of Physical Chemistry, University of Erlangen, Erlangen, Germany.

11:30 A.M.—"The Mechanism of Electrolytic Rectification" by H. E. Haring, Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

12:00 M.—"Anodic Polarization Because of Electron Deficiency" by M. E. Straumanis, University of Missouri, School of Mines and Metallurgy, Rolla, Mo.

2:00 P.M.—"Polarographic Study of the Kinetics of Irreversible Electrode Processes" by Paul Delahay, Department of Chemistry, Louisiana State University, Baton Rouge, La.

2:25 P.M.—"Hydrogen Overvoltage" by George Dubpernell and Roberta Dubpernell, Naugatuck Chemical Division, United States Rubber Company, Naugatuck, Conn.

2:50 P.M.—"Hydrogen Overvoltage of Bright Platinum" by Sigmund Schuldiner, Naval Research Laboratory, Washington, D. C.

3:15 P.M.—"Hydrogen Overvoltage on Smooth Platinum" by Ernest Yeager, T. S. Oey, and Frank Hovorka, Western Reserve University, Cleveland, Ohio.

3:40 P.M.—"Kinetics of Ionic Recombination and Implications in Hydrogen Overpotential Studies" by Paul Delahay, Department of Chemistry, Louisiana State University, Baton Rouge, La.

4:00 P.M.—"Mass Transfer in Electrode Processes, I. Techniques of Measurement" by M. Eisenberg, C. W. Tobias, and C. R. Wilke, Department of Chemistry and Chemical Engineering, University of California, Berkeley, Calif.

4:25 P.M.—"Mass Transfer in Electrode Processes, II. Free Convection at Vertical Plane Electrodes" by M. Eisenberg, C. W. Tobias, and C. R. Wilke, Department of Chemistry and Chemical Engineering, University of California, Berkeley, Calif.

Round Table

8:00 P.M.—Special Round Table on "Teaching of Electrochemistry."

Tuesday, May 6, 1952

Polarization (cont'd.)

Walter J. Hamer presiding

9:00 A.M.—"The A.C. Effects of Ultrasonic Waves on Polarized Gas Electrodes" by Ernest Yeager, H. J. Dietrick, and Frank Hovorka, Department of Chemistry, Western Reserve University, Cleveland, Ohio.

9:25 A.M.—"Irreversible Phenomena at Carbon Cathodes Depolarized by Gaseous Oxygen" by M. G. Jacobson, Mine Safety Appliances Company, Pittsburgh, Pa.

9:50 A.M.—"Polarization and the Thermodynamics of Irreversible Processes" by Pierre Van Rysselberghe, Department of Chemistry, University of Oregon, Eugene, Ore.

10:15 A.M.—"Alternating Current Electrolysis" by A. Edward Remick, Wayne University, Detroit, Mich.

10:40 A.M.—"Usefulness of the Thermodynamic Interpretation of Polarization Curves" by Marcel Pourbaix, University of Brussels, Brussels, Belgium.

11:05 A.M.—"Solubility and Diffusion of Hydrogen as a Factor in Its Overvoltage on Iron" by Arthur L. Pitman, Naval Research Laboratory, Washington, D. C.

11:30 A.M.—"Primary Current Distribution Around Capillary Tips Used in the Measurement of Electrolytic

Polarization" by Sidney Barnartt, Westinghouse Research Laboratories, East Pittsburgh, Pa.

11:55 A.M.—"Polarization Phenomena in Corrosion and Passivity of Iron in Aqueous Solutions" by Morris Cohen, National Research Council, Ottawa, Canada.

2:00 P.M.—"Information Concerning the Mechanism of Electrode Reaction as Provided by Current Reversal" by A. L. Ferguson, Department of Chemistry, University of Michigan, Ann Arbor, Mich.

2:25 P.M.—"Anodic Formation of Coatings on Magnesium, Zinc, and Cadmium" by Kurt Huber, Institute of Physical Chemistry, University of Bern, Bern, Switzerland.

2:55 P.M.—"The Electrochemical Behavior of Aluminum, III. In Buffered and Alkaline Solutions of Potassium Ferricyanide and in Sodium Hydroxide" by J. V. Petrocelli, The Patent Button Company, Waterbury, Conn.

3:20 P.M.—"Electrochemical Polarization of Titanium in NaCl Solution" by Colby D. Hall, Jr., and Norman Hackerman, Department of Chemistry, University of Texas, Austin, Texas.

3:45 P.M.—"Measurement of the Corrosion Rate of a Metal from Its Polarizing Characteristics" by W. J. Schwerdtfeger and O. N. McDorman, National Bureau of Standards, Washington, D. C.

4:10 P.M.—"Polarization of Copper Anodes in Chloride Solutions" by J. H. Bartlett and L. P. Stephenson, University of Illinois, Urbana, Ill.

4:35 P.M.—"The Overvoltage Effects at the Copper Electrode" by Thor Rubin, The Ohio State University, Columbus, Ohio.

Wednesday, May 7, 1952

General Theoretical Session

Paul Fugassi presiding

2:00 P.M.—"Standard States in Electrode Kinetics" by André J. deBéthune, Boston College, Chestnut Hill, Mass.

2:20 P.M.—"Thermogalvanic Potentials, II. Nickel in Neutral Nickel Sulfate Solution" by Dodd S. Carr and Charles F. Bonilla, The Johns Hopkins University, Baltimore, Md.

2:40 P.M.—"On the Origin of the Thermoelectric Potential Between Semiconductors of Different Impurity Levels and Semiconductors and Metals" by T. Forland and W. A. Weyl, Department of Mineral Technology, Pennsylvania State College, State College, Pa.

3:00 P.M.—"Chronopolarography: A Law of Conductivity" by J. G. Barredo, University of Chicago, Chicago, Ill.

3:30 P.M.—Round Table on Sign Convention with Norman Hackerman presiding. Panel members will be: H. H. Uhlig, Massachusetts Institute of Technology, Cambridge, Mass.; L. B. Rogers, Massachusetts Institute of Technology, Cambridge, Mass.; André J. deBéthune, Boston College, Boston, Mass.; and Pierre Van Rysselberghe, Department of Chemistry, University of Oregon, Eugene, Ore.

Thursday, May 8, 1952

General Theoretical Session (cont'd.)

Paul Fugassi presiding

9:00 A.M.—"An Electrochemical Method for Oxygen Determination" by M. G. Jacobson, Mine Safety Appliances Company, Pittsburgh, Pa.

9:25 A.M.—"Wet Type of Photovoltaic Cells: Classification, Mechanism on the Uncoated Electrode Type" by A. B. Garrett, Wallace Copeland, Paul Clark, Otis Black, and John Bocher, Department of Chemistry, The Ohio State University, Columbus, Ohio.

9:50 A.M.—"The Nature of Passivity Films Formed on Iron by Solutions of Sodium Phosphate" by M. J. Pryor, F. Brown, and M. Cohen, National Research Council, Ottawa, Canada.

10:15 A.M.—"Factors Affecting the Potential of the Silver-Silver Chloride Electrode" by D. N. Staicopoulos, H. J. Dietrick, and Frank Hovorka, Department of Chemistry, Western Reserve University, Cleveland, Ohio.

10:40 A.M.—"Some Properties of Stannous Sulfate Solutions and Their Role in Electrodeposition of Tin, I. Solutions with Only Stannous Sulfate Present" by C. A. Discher, Rutgers University, College of Pharmacy, Newark, N. J.

11:05 A.M.—"Electrodeposition Behavior of Cadmium and Thallium at a Mercury Cathode" by L. B. Rogers and Charles Merritt, Jr., Department of Chemistry and Laboratory of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

11:30 A.M.—"Factors Affecting the Direct Current Resistance of Electrolytes" by D. MacGillavry, Department of Chemical Engineering, Columbia University, New York, N. Y.

11:55 A.M.—"Ion Exchange Membranes in Electrolytic Processes" by George W. Bodamer, Alvin G. Winger, and Robert Kunin, The Rohm and Haas Company, Philadelphia, Pa.

12:20 P.M.—"Membrane Potential of Ion-Exchange Resins" by Sakae Tajima and Yujiro Kosaka, Department of Industrial Chemistry, Tokyo Metropolitan University, Tokyo, Japan.

General Theoretical Session (cont'd.)

Conductivity and Electrolytes

Walter J. Hamer presiding

2:00 P.M.—"Conductivity and Transference in Molten Salt Systems" by Frank E. W. Wetmore, Electrochemical Laboratory, University of Toronto, Toronto, Canada.

2:25 P.M.—"Electrical Conductance and Viscosity in Highly Concentrated Salt Solutions" by Ralph P. Seward, School of Chemistry and Physics, Pennsylvania State College, State College, Pa.

2:50 P.M.—"The Acid Dissociation of the Aquo Scandium Ions" by Martin Kilpatrick and Lewis Pokras, Department of Chemistry, Illinois Institute of Technology, Chicago, Ill.

3:15 P.M.—"The Acid Strengths of the Phenylacetic Acids" by Mary Kilpatrick and E. A. Fackenthal, Department of Chemistry, Illinois Institute of Technology, Chicago, Ill.

3:35 P.M.—"Conductivities and Densities of the System Ammonium Chloride—Zinc Chloride—Methanol from −50° to 20° C" by L. R. Dawson, P. G. Sears, G. P. Dinga, and H. K. Zimmerman, Jr., University of Kentucky, Lexington, Ky.

3:55 P.M.—"Ion Association in 2-1 Salts in Methanol" by F. Muriel Sacks and Raymond M. Fuoss, Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

4:20 P.M.—"Electrically Conducting Films of Hydrolyzed Tin Chloride" by Robert R. Ralston and Duncan C. Blanchard, Transformer and Allied Products Division Laboratory, General Electric Company, Pittsfield, Mass.

4:55 P.M.—"The Electrical Conductance of Solutions of Cobalt (II) Nitrate Hexahydrate in Acetophenone at 25°C" by Charles C. Templeton and Kurt H. Stern, Exploration and Production Research Division, Shell Oil Company, Houston, Texas.

Earl Gulbransen, Starr Thayer Receive 1952 NACE Awards

Earl A. Gulbransen, advisory engineer to Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania, and Starr Thayer, a cathodic protection consultant of Houston, Texas, have been designated to receive the 1952 annual Frank Newman Speller and Willis Rodney Whitney Awards from the National Association of Corrosion Engineers. The awards were presented at the annual banquet of the association held on March 13, during the Eighth Annual Conference and Exhibition at Galveston, Texas. The Speller award is given for achievement in corrosion engineering; the Whitney award for corrosion science.

Mr. Gulbransen, whose principal scientific interests are in the high temperature field, joined Westinghouse Research Laboratories in 1940. A graduate of State College of Washington in chemical engineering in 1931, he later obtained a Ph.D. in physical chemistry from the University of Pittsburgh. He has been a teacher of chemistry and chemical engineering.

Author of many papers, Mr. Gulbransen was consultant during World War II to the Government on new methods of underwater propulsion. He is a member of The Electrochemical Society and is currently Regional Editor for the JOURNAL. He has held a number of offices in the Society and, in addition, has been chosen many times as chairman of national meetings for various scientific groups.

Mr. Thayer, among the first engineers to apply cathodic protection to underground structures, is a 1908 graduate in electrical engineering from Iowa State College. Since 1931 he has installed many cathodic protection systems in this country and abroad. He is, at present, a consultant in this field.

An Open Letter to the Membership

At the meeting of the Board of Directors, on January 25, 1952, I recommended to the Board that it consider increasing the membership dues for 1953 from $12 per year to $15 per year. This letter is to explain my reasons to you for this action.

The dues of the Society are defined in the bylaws. The bylaws can be amended by the Board of Directors at its discretion, provided that the proposed amendment is placed on the table until the next meeting. The Board will, therefore, consider raising the dues at the Philadelphia meeting in May.

This subject is not new to you. An open letter regarding finances was published in the July 1951 issue of the JOURNAL and, during the year when I have attended Section Meetings, it has been called to your attention that for several years the Society has been operating in the red.

The budget which we adopted for 1952 called for $66,900 expenditures and $64,300 income. This budget anticipates $10,000 income from advertising if $64,300 is to be collected. In my July letter I told you that we hoped to receive $5,000 worth of advertising during 1951—actually, we got $3,198. This was a big improvement over 1950, but still was below what we needed.

Our dues were increased two years ago from $10 to $12 per year. This was only a 20 per cent increase, whereas other organizations at the same time were making 40 to 50 per cent increases.

Your Board, at that time, sincerely thought that the $2.00 increase would be ample, but costs have continued to increase, advertising has not been up to our expectations and, as a result, during the last few years when we should have been building up a reserve, we have had several years of deficit.

It is my belief that our deficit for 1951 operations will be about $4,600. This, spread over our membership, is a little over $2 per member. Other members of the Board feel that the deficit will be less, and will be slightly over $1 per member. If we increase the dues to $15 per year, this should give us a little leeway if prices continue to rise.

The Society believes that it is furnishing its members with improved service in the office, we know that we are publishing a constantly improving JOURNAL, we have plans and hopes for extending our Weston Fellowship, and the Local Sections are asking us for more financial assistance. All of these things require money.

If you believe the Board is making a wise move in increasing the dues, let its members, through the Secretary, know your feelings. It is only by hearing from you, that we understand how you feel.

RALPH M. HUNTER

1952 ASTM Lecturers

Two important lectures have been scheduled for the Fiftieth Anniversary Meeting of the American Society for Testing Materials, to be held in New York City during the week of June 23, 1952.

On Monday, June 23rd, Dr. R. C. McMaster, Battelle Memorial Institute, will deliver the 26th Edgar Marburg Lecture on the subject, "Non-destructive Testing." The first H. W. Gillett Memorial Lecture is to be given by Dr. N. L. Mochel, Westinghouse Electric Corporation. It will be presented on Wednesday, June 25th, at which time Dr. Mochel will discuss "Man, Metals and Power."

Corrosion Symposium by Chemical Engineers

"Corrosion" will be the topic of a symposium sponsored by six local sections of the American Institute of Chemical Engineers on April 21 at the Mayflower Hotel, Akron, Ohio. A series of six papers will be presented, as follows:

James A. Lee—Keynote Address.

R. M. Burns—"Studies of Corrosion Reactions."

Mars Fontana—"New Commercial Metals and Alloys for Corrosion Resistance."

W. E. Friend—"Design of Equipment from the Standpoint of Corrosion Resistance."

R. B. Hoxeng—"Corrosion of Ferrous Metals."

Speaker from Dow Chemical Company—"Cathodic Protection."

Robert C. Stell of Goodyear Tire & Rubber Company and Walter M. Otto of Firestone Tire & Rubber Company are co-chairmen of the symposium.

Monsanto to Build Phenol Plant

Plans have been announced for the construction of a new plant at Avon, California, for the manufacture of phenol. The plant will be jointly built and operated by Monsanto's Western and Organic Chemicals Divisions. The phenol, to be produced by a process recently developed by the company, will be sold on a contract basis to various firms in the growing Pacific coast industrial area. It will also be used by Monsanto to meet the expanding needs of its own western manufacturing operations. Construction is expected to begin at approximately midyear, and production will commence early in 1954.

Blum Retires; Brenner Heads Electrodeposition Section of National Bureau of Standards

WILLIAM BLUM

Dr. William Blum, internationally known for his contributions to the field of electrochemistry, retired on January 1st as Chief of the Electrodeposition Section of the National Bureau of Standards. He has been succeeded by Dr. Abner Brenner.

Dr. Blum joined the Bureau in 1909 and has been responsible for NBS research and development in the field of electrochemistry since 1929. He has done research in electrodeposition, including electroplating, electrotyping, and electroforming.

Many of his technical papers are in the field of electrodeposition; also, he is the author of chapters in several corrosion handbooks and of the revised third edition of the text, "Principles of Electroplating and Electroforming."

Honorary memberships have been conferred on Dr. Blum by the Electrodepositers' Technical Society of London and by the American Electroplaters' Society. He has been awarded the Acheson Medal and the Medal of the Institute of Chemistry for Distinguished Governmental Service.

Dr. Blum is a past president of The Electrochemical Society and has held many offices in the Society. He has also been active in other organizations.

Dr. Brenner has been engaged in electrodeposition research at the Bureau since 1930, and has conducted extensive investigations of alloy deposition, especially tungsten and molybdenum with iron, nickel, and cobalt, and on the nature of cathodic films.

ABNER BRENNER

Dr. Brenner is the author of many technical papers in the electroplating field and is the inventor of the magnegate, an instrument for measuring the thickness of plated coatings, and of the spiral contractometer, and he has developed a process for the purification of rhodium plating solutions.

He is currently a Divisional Editor of the JOURNAL of The Electrochemical Society, and is a member of a number of leading scientific societies.

Facilities for Producing Graphite Electrodes

Ground has been broken to start the construction of new graphitizing facilities which will greatly increase the production of graphite electrodes at the Niagara Falls plant of International Graphite and Electrode Corporation, a subsidiary of Speer Carbon Company, St. Marys, Pennsylvania. Costing $10,000,000, the expansion is being undertaken by IGE to meet the increasing demand of the electric steel and chemical industries. The new facilities will include a calciner, 16 graphitizing furnaces, and complete milling, extruding, and baking facilities. Full production is expected to being in May 1953.

Silver Refinery in India

The Government of India has completed plans for starting a silver refinery, the first of its kind in Asia, in 1953 at Calcutta. This refinery, when in operation, is expected to handle the refining of silver from countries outside India. It is intended for the extraction of about 300 million ounces of silver from coins which were introduced during World War II and are now being replaced by nickel coins. The project is expected to save India a sum of Rs. 5 crores ($10,000,000.). T. L. R. C.

India's Chemical Industry Aided by U. S. Company

Under a unique India-American business arrangement, India's first dyestuff and pharmaceutical plant begins operation this month at Bulsar, near Bombay, American Cyanamid Company officials have announced.

The new company, known as Atul Products Ltd. was made possible by the merger of Indian capital and the technical "know-how" of the American Cyanamid Company. Under their arrangement, 90 per cent of Atul's capital is subscribed by India's bankers and businessmen. American Cyanamid invested 10 per cent at the request of the Indians as a tangible token of its serious interest in Atul's 20-year program for development of a full scale Indian chemical industry aimed at making the country independent of outside supply sources for its major needs. At the beginning, American Cyanamid will supply technical assistance and personnel, and will also provide some raw materials.

One potential of the new industry is its plan to produce enough sulfa drugs to cure most of the infectious diseases which seriously hamper the nation's economic progress. It will also produce enough of the 20 to 25 more popular dyestuffs to supply the country's textile, paper, and other firms which require these.

MEETINGS OF OTHER ORGANIZATIONS

GREATER NEW YORK SAFETY COUNCIL, 22nd annual safety convention & exposition, Hotel Statler, New York City, April 1–4.

AMERICAN SOCIETY FOR TESTING MATERIALS, annual meeting, fiftieth anniversary, Hotel Statler and New Yorker, New York City, June 23–27.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS, summer general meeting, Hotel Nicollet, Minneapolis, Minn., June 23–27.

Cleveland Section Contest Winners

The Cleveland Section of The Electrochemical Society recently sponsored a contest among the nine colleges in the Cleveland area for the purpose of

GERALD S. LOZIER

increasing the interest in electrochemistry at the undergraduate level. On the basis of nominations made by the faculties of their respective institutions, the following two students were chosen to receive awards, in each case a one-year Student Associate Membership in-

EDWIN J. SIEGMAN

cluding a subscription to the JOURNAL of The Electrochemical Society.

Gerald S. Lozier was class valedictorian at Lakeville, Ohio, High School and received an Ohio District State Scholarship award ranking fourth in the state in chemistry and seventh in physics with honorable mention in biology and plane geometry. He is a senior at Western Reserve University where he has held a full tuition scholarship and a student assistantship in chemistry. During the current semester, he will be doing research in electrochemistry under the joint direction of Dr. Frank Hovorka and Dr. E. B. Yeager.

Edwin J. Siegman, a graduate of Cathedral Latin High School, Cleveland, is a senior in Chemical Engineering at Case Institute of Technology. He is president of the Gamma Chapter of Alpha Chi Sigma, a member of Tau Beta Pi, and is a student member of the American Institute of Chemical Engineers and the American Chemical Society.

The presentation of the membership certificates was made at a subsequent meeting of the local section. The committee in charge of this contest consisted of G. W. Heise, Chairman, J. M. Margolis, and F. Keller.

SECTION NEWS

New York Metropolitan Section

Norman H. Hackerman, Professor of Chemistry at the University of Texas, and Technical Editor of the JOURNAL, spoke before the New York Metropolitan Section at its meeting on February 19th at the Holley Hotel. A social hour and dinner preceded the technical meeting.

Dr. Hackerman spoke on "Corrosion," and his talk was particularly concerned with the nature of the surface of metals, and the mechanism of electron and ion transfer through surfaces. Experiments were described which featured the use of "tagged" chromium in the investigation of the adsorption of chromium on steel surfaces. These experiments tended to show that the amount of chromium adsorbed is sufficient to produce a layer one atom thick. Considerable discussion followed the presentation.

A feature of the meeting was the presence of Dr. Blum, who obliged with a few remarks and who also contributed considerably to the discussion of Dr. Hackerman's paper.

F. A. LOWENHEIM, *Secretary*

San Francisco Section

Charles W. Tobias, of the Department of Chemistry and Chemical Engineering, University of California, Berkeley, California, was the guest speaker at the January 16th meeting of the San Francisco Section. His subject was "The Production of Ozone by the Electrolysis of Sulfuric Acid."

Dr. Tobias began his talk, which was well illustrated by slides, by reviewing the history of ozone production. He described the only commercial method for the production of ozone currently used. This process, known as the silent discharge method, has a low yield and is very expensive both from the standpoint of floor space requirements and cost of equipment. It has made the use of ozone as an oxidizing agent very limited except in special cases. Anodic ozone evolution has been known for over 100 years but there was not much success in developing a useful process until the early 1900's. Since then, considerable work has been done but the conclusions drawn have been in disagreement.

Dr. Tobias then described the experimental work being done at the University of California. The reaction involved is:

$$3H_2O = O_3 + 6H^+ 6e^- \quad (E_0 = -1.504 \text{ volts})$$

The following conditions are pertinent to the cell used and its operation: (1) platinum anode cooled to −60°C, (2) lead cathode, (3) glass cloth diaphragm, (4) sulfuric acid electrolyte, and (5) current density of 0.5-0.75 amp per cm^2.

The best results obtained thus far are a 32 per cent O_3 yield with a sulfuric acid solution of 1.20 sp gr. Lower acid concentrations produce a better yield but the electrolyte freezes. Higher anode temperatures cause catalytic decomposition of the ozone product. The catalyst in this reaction is the platinum anode.

Further development work is being carried on at the present time with the design of a cell suitable for industrial use as an ultimate objective.

An interesting discussion followed Dr. Tobias' talk and all who attended enjoyed the meeting greatly.

R. F. BECHTOLD, *Secretary-Treasurer*

PERSONALS

GEORGE W. JERNSTEDT has been appointed manager of engineering for the Special Products Development Division of Westinghouse Electric Corp., Pittsburgh, Pa. He will continue in charge of Electroplating Projects, in addition to his new appointment.

K. SESHADRI has been awarded the Ph.D. degree in science by the Benares Hindu University, Benares.

M. S. THACKER has returned from his tour in the United States as special guest from India at the invitation of the U. S. Government. He visited several institutions and engineering projects during this trip.

ELEANOR REID RESIGNS

Miss Eleanor Reid, Managing Editor of the *Journal*, resigned her position, effective February 15, to be married. She had been with the *Journal* for four years. On March 8, at her home in Wake Forest, North Carolina, Miss Reid was married to Brian Derek Forrow of New York. As Mr. Forrow is now with the Air Force, stationed at Mountain Home, Idaho, the couple will reside there for the present.

RUTH STERNS JOINS JOURNAL STAFF

Mrs. Ruth Garrett Sterns was appointed Assistant Editor of the JOURNAL starting February 1. Mrs. Sterns was previously on the editorial staff of *Mining Engineering* and its predecessor, *Mining and Metallurgy*. Included in her duties on the *Journal* will be the preparation of copy, contacts with authors, and supervision of general production work.

ALBERT J. HAM of Shell Lubricating Oil Laboratories, Chester, England, is now at the Thornton Research Centre, in Chester.

GUILLIAM H. CLAMER, president of the Ajax Group Companies, Philadelphia, and WILLIAM A. DARRAH, president of Continental Industrial Engineers, Inc., Chicago, were recipients of the Trinks Industrial Heating Awards presented at the meeting of the Industrial Furnace Manufacturers Association, in Pittsburgh, on January 21st.

GEORGE E. GOODRICH has been appointed assistant manager, industrial department, of Westinghouse Electric Corp.'s Apparatus Division, Pittsburgh, Pa. Prior to this promotion, Mr. Goodrich was resale manager of the company's Middle Atlantic District with headquarters in Philadelphia.

V. ARAVAMUTHAN has been appointed Senior Research Assistant in a program sponsored by the Atomic Energy Commission in India; the work is to be carried out at the Indian Institute of Science, Bangalore.

EDGAR C. PITZER, General Electric Company, Schenectady, N. Y., has been transferred to the Hanford Engineering Works, Pile Technology Division, where he will be concerned with certain electrochemical and metallurgical problems.

MILTON J. ALLEN has joined the staff of the CIBA Research Laboratories, Summit, N. J. Dr. Allen was previously connected with the National Cancer Institute, Bethesda, Md.

S. KRISHNAMURTHY has been awarded the Ph.D. degree in science by the University of Bombay, Bombay.

JOHN MCCALLUM is now employed as electrochemical engineer at Battelle Memorial Institute, Columbus, Ohio. Mr. McCallum came from Eastman Kodak Company, Rochester, N. Y.

GWYN BENSON of Shawinigan Falls, Montreal, director of plant research for Shawinigan Chemicals Limited since 1944, has been appointed European technical representative for that company, and left for his headquarters in London early in March. Mr. Benson will travel throughout the western parts of the Continent, studying processes and keeping in touch with new chemical developments there.

FRED M. BERKEY has been appointed a supervisor in the engineering sales department of Monsanto Chemical Company's Organic Chemicals Division, St. Louis, Mo.

NEW MEMBERS

In February 1952, the following were elected to membership in The Electrochemical Society:

Active Members

JOHN R. ALBERT, T. C. Wheaton Company, mailing add: North Delsea Dr., Route No. 3, Millville, N. J. (Battery, Electrodeposition, Electronics, and Theoretical Electrochemistry)

ANTHONY JOHN ANDREATCH, Naval Research Laboratory, mailing add: 5826 31st Place, West Hyattsville, Md. (Battery, Electronics, and Theoretical Electrochemistry)

CYRO PULINO DE CAMARGO, Instituto Tecnologico de Aeronautica, mailing add: Rua Martim Francisco 263, Sao Paulo, Brazil (Theoretical Electrochemistry)

CLAIRE HOWE FELLOWS, The Detroit Edison Company, 2000 Second Ave., Detroit 26, Mich. (Corrosion, Electric Insulation)

HENRY LEONARD GILBERT, U. S. Bureau of Mines, mailing add: 542 N. 29 St., Corvallis, Ore.

GEORGE W. HEALY, Union Carbide

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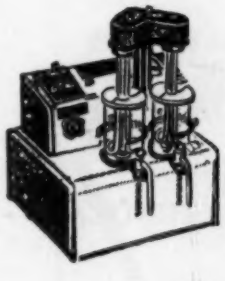

For determination of aluminum in steel, aluminum in zinc base alloys, and other separations—DYNA-CATH is a completely new high speed mercury cathode apparatus which accelerates and does a more complete job in the analytical separation of metals. For example, DYNA-CATH quantitatively removes 5 grams of iron from 100 ml. of electrolyte in 60 minutes. It overcomes the difficulties which have prevented utilization of the mercury cathode as an analytical tool.

Write for Bulletin 220.

Eberbach CORPORATION
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and Carbon Research Laboratories, Inc., Electrometallurgical Division, Niagara Falls, N. Y. (Electrothermic)

EUGENE RAYMOND KUCZYNSKI, Leeds & Northrup Company, 4901 Stenton Ave., Philadelphia 44, Pa. (Electronics)

VERNON A. LAMB, National Bureau of Standards, Electrodeposition Section, Washington 25, D. C. (Corrosion, Electrodeposition)

Electroplaters!

The Los Alamos Scientific Laboratory is accepting applications for the following openings:

1. An Electroplating Shop Supervisor with several years of wide experience in the electroplating field, preferably in laboratory work. A college degree in chemistry or chemical engineering is essential. Duties include working with ferrous, non-ferrous, rare metals, and non-conductors; testing; and supervision of a small electroplating shop.

2. A technician-operator for the electroplating shop. Must have knowledge and experience in various electroplating techniques.

Write to Personnel Department, University of California, Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico.

HENRY P. LANGSTON, Springfield Armory, Springfield 1, Mass., mailing add: 44 Garden St., Springfield, Mass. (Theoretical Electrochemistry)

PETER JAMES LIBRIZZI, Allen B. DuMont Laboratories, Clifton, N. J., mailing add: 66 Mohr Ave., Bloomfield, N. J. (Electronics)

TADAYUKI NAKAYAMA, c/o Scientific Research Institute, Ltd., Komagome Bunkyo-ku, Tokyo, Japan. (Corrosion)

EARL F. SENKBEIL, Milwaukee Gas Specialty Company, P. O. Box 461, Milwaukee 1, Wis. (Electrodeposition)

JOSEPH H. SIMONS, The University of Florida, mailing add: 1122 S. W. Eleventh Ave., Gainesville, Florida. (Industrial Electrolytic and Theoretical Electrochemistry)

HAROLD SMALLEN, U. S. Naval Ordnance Test Station, 60-A Rowe St., China Lake, Calif. (Electrodeposition)

BERNARD JUNIOR STURM, Materials Chemistry Division, Oak Ridge National Laboratory, mailing add: Chester Hall, Oak Ridge, Tenn. (Battery and Corrosion)

PAUL N. TAGGETT, General Electric Company, Syracuse, N. Y., mailing add: 123 Millen Dr., No. Syracuse, N. Y. (Electronics)

S. J. WALLDEN, Boliden Mining Company, Skelleftehamn, Sweden. (Battery, Electrodeposition, Electrothermics and Industrial Electrolytic)

SHIGETO YAMAGUCHI, c/o Scientific Research Institute, Ltd., Komagome Bunkyo-ku, Tokyo, Japan. (Corrosion)

JOHN H. ZAUNER, c/o Eureka Williams Corporation, Bloomington, Ill. (Battery)

RAY A. ZIMMERLY, Columbia Steel Company, mailing add: 1524 Maynard St., Concord, Calif. (Corrosion and Electrodeposition)

Student Associate Members

GERALD S. LOZIER, Western Reserve University, mailing add: 2085 Adelbert Rd., Cleveland 6, Ohio. (Electrodeposition)

EDWIN J. SIEGMAN, Case Institute of Technology, mailing add: 993 Pembrook Rd., Cleveland Heights 21, Ohio.

Reinstatements

GUSTAV DOBRIN, Perrine Quality Products Corp., 55 Rumford Ave., Waltham 54, Mass.

JACQUES L. BROAD, Lauderdale Plating, 522 N. E. First Ave., Ft. Lauderdale, Fla.

ARNE J. MOLLER, Danmarks Tekniske Bibliotek, 10, Oster Voldgade, Copenhagen K, Denmark.

LITERATURE FROM INDUSTRY

PHANTOM REPEATER. 4-page bulletin describes Model 102 Phantom Repeater, a bridging amplifier with an extremely high input impedance, which is used to increase the accuracy of vacuum tube voltmeters and oscilloscopes on high impedance circuits. Complete specifications listed, including diagrams of applications, etc. Keithley Instruments. P-20

X-RAY DIFFRACTION & SPECTROMETRIC EQUIPMENT. New 60-page catalogue titled "X-Ray Diffraction and Geiger-Counter X-Ray Spectrometric Equipment" has been released. In addition to x-ray diffraction, spectrometry and fluorescence analysis, the catalogue also includes such components and accessories as tubes, rectifiers, and cameras, sections on camera mounting brackets, film illuminaters, etc. North American Philips Co., Inc. P-21

HIGH FREQUENCY POWER SUPPLY. Circular describes new 400-Cycle Motor-Alternator, meeting AN-E-19 requirements for power supplies. Offers marked freedom from maintenance, utilizes no rotating coils, requires no brushes or springs, is small in size and unusually compact. American Electric Motors. P-22

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FHP MOTORS. Bulletin and fact sheet gives information on new line of fractional horsepower motors embodying an entirely new concept of motor design and manufacture. Motors are available in open drip-proof and totally enclosed fan-cooled models; these have hundreds of applications—on pumps, fans, blowers, compressors, office and home appliances, etc. General Electric Company. P-23

INDUSTRIAL FURNACES. New 38-page booklet, entitled "Harnessing Heat," tells how to match a furnace to your particular heat-treating problem. Twelve different types of furnaces—both gas and electric—are described and their chief fields of application outlined. Sections devoted to special furnaces and protective atmospheres. Westinghouse Electric Corp. P-24

ELECTROMETER. An improved vacuum tube electrometer (Model 200A) at no increase in price makes possible more closely overlapping scale ranges and greater accuracy. Literature available. Keithley Instruments. P-25

SELENIUM RECTIFIERS. Illustrated catalogue, "A Guide to Better Plating Power," describes complete line of Sel-Rex Selenium Rectifiers. Includes all types of rectification to provide d-c power for every electroplating, electropolishing, electrocleaning, and electrochemical need. Bart-Messing Corp. P-26

LABORATORY EQUIPMENT. New edition of "Laboratory" contains illustrated descriptions of new laboratory instruments, apparatus, and techniques. Also articles of general scientific interest. Fisher Scientific Co. P-27

SISALIN SECTIONS. Two-color bulletin on Sisalin Sections for *both* buffing and polishing tells how Sisalin Sections of unbleached muslin and sisal can be used for eight different polishing and buffing operations; gives specifications and includes field performance information. Hanson-Van Winkle-Munning Co. P-28

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

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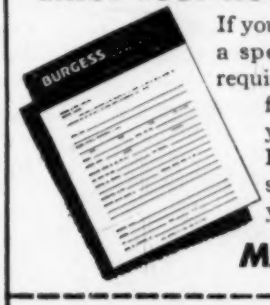

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Highlights of the Board of Directors' Meeting

(Held January 25, 1952)

The auditor's report for the fiscal year January 1, 1951, to December 31, 1951, was accepted. The Balance Sheet and Analysis of Expenditures and Income are shown below. It should be noted that the expenditures exceeded receipts by $5,679.09. However, $3,342.93 was spent to publish Volumes 95, 96, and 97, money for which was collected during previous years for this purpose. Also, a major portion of the item of "Furniture and Office Equipment" amounting to $2,187.61 is represented by the purchase of new addressograph equipment, which should be amortized over several years. It should also be noted that the Audit shows income and expenditures for the Corrosion Division. These are funds handled by the National Office for the Division.

The budget which follows, showing the operation of our 1951 budget and the expected requirements for 1952, was adopted.

The need for increasing dues and subscription rates was then discussed. Since the rates are fixed by the bylaws, it is necessary that prior notice be given before they can be altered. Due notice, therefore, was given that at the Philadelphia Meeting, May 4, 1952, the Board will consider a proposal to increase dues and subscription rates.

Walter H. Prine, Chairman of the Sustaining Membership Committee, reported that since our last Board meeting, held in Detroit, four new sustaining members have joined the Society. These are: Air Reduction Company, Inc., New York, N. Y.; E. I. du Pont de Nemours & Company, Inc., Towanda, Pa.; Kaiser Aluminum and Chemical Corporation, Spokane, Wash.; and McGean Chemical Company, Cleveland, Ohio.

On the recommendation of Mr. Frank LaQue, it was decided to offer the bound Anniversary volume (1952) to members at the rate of $6 each, if orders are received before December 15, 1952. After this date, the rate will be $15, the same as to nonmembers.

The advisability of publishing a Ten-Year Index was discussed at some length. Since the cost will be rather high, the Secretary was instructed to poll the membership as to their desire to obtain such an index at a cost not to exceed $10.

A very complete report by the Managing Editor was presented by Dr. Burns, after which he presented Miss Eleanor Reid's resignation, effective February 15, 1952. The reason for this resignation was that Miss Reid planned to be married in the spring. The Board gave her a unanimous vote of thanks for her fine work on the JOURNAL for the last four years.

Dr. Burns then announced the appointment of Mrs. Ruth Sterns as Assistant Editor, to start work on February 1, 1952, so that continuity in the Editorial Office will be maintained.

HENRY B. LINFORD, *Secretary*

Auditor's Report

BALANCE SHEET

December 31, 1951

Assets

Furniture and Office Equipment	$ 4,242.61	
Cash	12,528.39	(a)
U. S. Savings Bonds (Cost)	28,860.00	(b)
Inventory—Bound Volumes	4,850.48	
Accrued Income on U. S. Savings Bonds	4,212.00	
	$54,693.48	

Liabilities, Reserves, and Surplus

Accounts Payable—Suppliers	$ 2,581.67	
Taxes Withheld from Salaries	273.00	
Life Memberships	1,519.47	
Prepaid Sustaining Memberships	100.00	
Prepaid Subscriptions	2,854.00	
Reserve for Depreciation	428.18	
Surplus	46,937.16	(c)
	$54,693.48	

(a) Includes: $1,918.68 Corrosion Division Fund

(b) Includes: $10,471.37 Corrosion Division Fund; $400.00 Columbus Convention Committee Fund

(c) Includes: $12,790.05 Applicable to Funds Detailed in (a) and (b).

EXPENDITURES

Furniture and office equipment			$ 2,187.61
Publication Department			
General Expenses			
Salaries, full-time employees	$10,183.90		
Wages, part-time employees	209.00		
Rent	810.00		
Stationery and supplies	533.42		
Postage and express	455.57		
Traveling	389.51		
Miscellaneous office expenses	612.35	$13,193.75	
Publication expenses			
Journal	$19,330.54		
Volumes: 95	512.30		
96	1,923.56		
97	907.07		
Membership Directory	607.78		
Reprints	2,389.87	$25,671.12	
Secretary's Department			
Salaries, full-time employees	$12,373.10		
Wages, part-time employees	302.05		
Rent	810.00		
Stationery and supplies	1,244.49		
Postage and express	1,352.49		
Traveling	423.68		
Miscellaneous office expenses	892.87		
Faraday Society	2,266.97		
Audit	160.00		
Prizes	100.00		
Local Sections:			
Philadelphia	182.00		
Metropolitan	257.00		
Midland	66.50		
Cleveland	119.00		
Washington-Baltimore	92.50		
Pittsburgh	50.00		
Detroit	78.50		
Electric Insulation Division	20.00		
Theoretical Electrochemistry Division	50.00		
Conventions	1,347.98		
Publication Committee	205.00		
Corrosion Division	2,033.80		
Emblems	30.79	$24,458.75	
Total			$65,511.36

Income

Dues: 1949	$ 10.00
1950	92.30
1951	10,114.30
1952	14,671.99
1953	12.00
1954	12.00
Volumes: 1950	4.00
1952	24.00
Publications	1,935.58
Membership Directory	580.00
Reprints	2,606.47
Preprints	133.08
Journal	491.38
Modern Electroplating	848.89
Thompson Monograph	44.15
Cathodic Protection	779.90
Deutschen Bunsengesellschaft	216.00
Faraday Society	2,096.84
Subscriptions: Journal	10,249.12
Volumes	322.80
Sustaining Memberships	5,650.00
Advertising	4,087.25
Conventions	2,847.78
Corrosion Division	1,774.80
Emblems	81.00
Interest	146.48
Total	$59,832.11
Excess expenditures over income	$ 5,679.09
Accounted for as follows:	
Surplus (reduction)	$ 3,491.48
Furniture and Office Equipment	2,187.61
	$ 5,679.09

(Signed) H. K. Leicht, Auditor

Analysis of Budgets for 1951 and 1952

Income

	Budget, 1951	*Actual, 1951*	*Proposed Budget, 1952*
Membership Dues	$25,000	$24,913	$27,500
Sustaining Memberships	6,000	5,650	6,700
Sale of Publications:			
Back Transactions	$ 2,500	$ 2,262	$ 1,600
Reprints & Preprints	2,500	2,740	3,000
Nonmember Journal Subscriptions	8,000	10,249	10,000
Office Sale Journal	400	491	500
Modern Electroplating	600	849	400
Royalties—"Cathodic Protection"	800	780	400
Deutschen-Bunsengesellschaft	300	216	200
Faraday Society—ECS Journal Subs.	500		500
Faraday Society Transactions	1,750	2,097	2,000
	17,350	19,684	18,600
Convention Registration	3,000	2,848	1,500
Advertising	3,500	4,087	10,000
	$54,850	$57,182	$64,300
Nonbudgeted—1952 Volumes			36

Expenditures—Publication

Printing & Mailing Journal	$22,000	$19,331	$24,000
Reprints	2,000	2,390	2,500
Salaries	10,200	10,390	12,000
Rent	855	810	810
Postage, Supplies, & Misc.	1,500	1,601	1,500
Travel	500	390	250
Publication Committee	325	205	250
	$37,380	$35,117	$41,310
Nonbudgeted—1952 Volumes			400

Expenditures—Secretarial

Salaries	$12,184	$12,675	$14,000
Rent	855	810	810
Postage, Supplies, & Misc.	3,100	3,490*	3,000
Travel	400	424	500
Auditor	175	160	180
Local Sections & Divisions	900	915	1,000
Prize to Young Authors	100	100	100
Program Booklets & Convention Material	1,400	1,348	1,400
Faraday Society	1,750	2,267	2,000
	$20,864	$22,189	$22,990

Summary of Budgeted Income and Expenditures

Income	$54,850	$57,182	$64,300
Expenditures	58,244	57,306	64,300

Nonbudgeted Income

Thompson Monograph	$ 44
Emblems	81
Interest	146
Corrosion Division	1,775
Membership Directory	580
Bound Volume—1952	24
Total	$ 2,650
Total Budgeted Income	57,182
Total Income	$59,832

Nonbudgeted Expenditures

Addressograph Equipment, etc.	$ 2,188
Directory	608
Back Volumes	3,344
Corrosion Division	2,034
Emblems	31
Total Nonbudgeted Exp.	8,20
Total Budgeted Exp.	57,30
Total Expenditures	$65,51

SUMMARY OF OVER-ALL OPERATION OF SOCIETY FOR THE YEAR 1951

Total Budgeted Income	$57,18
Total Nonbudgeted Income	2,63
Total Income	59,82
Total Budgeted Expenditures	57,30
Total Nonbudgeted Expenditures	8,20
Total Expenditures	65,51
Excess Expenditures Over Income	$ 5,67

* Includes { 233.58 penalty and interest a/c delinquent return W/H tax for 1st and 2nd quarters 1948; 200.00 for 2 printings "Aims and Activities" booklet

RECENT PATENTS

Selected for electrochemists by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

December 4, 1951

Camin, E. L. A., Hybinette, S. E., and Taylor, H. B., 2,576,922, Electrodeposition with Nickel

Chester, A. E., 2,576,997, Acid Zinc Electroplating and Electrolyte Therefor

Main, R. F., and Hansen, H. F., 2,576,998, Method of Electroplating Zinc

Chester, A. E., Main, R. F., and Hansen, H. F., 2,576,999, Method of Electroplating Zinc

Smith, A. L. J., 2,577,161, Cerium Activated Calcium-Magnesium Silicates

Rios, K. J., 2,577,209, Infrared Release of Water of Crystallization

Reid, F. H., 2,577,364, Rhodium Plating

Reid, F. H., 2,577,365, Rhodium Plating

Bartlett, K. M., 2,577,644, Apparatus for Anodically Treating Internal Surfaces

Proff, P. H., and Murphy, L. G., executor of said Proff, P. H., deceased, 2,577,714, Battery Cable Clamp

December 11, 1951

Westby, G., 2,577,833, Process for Electrowinning Chromium

Tichenor, R. L., 2,578,027, Storage Battery Charging System and Method

Coleman, E. D., 2,578,044, Electrode Structure

Miller, J. R., 2,578,145, Apparatus for Handling Liquids

Longaker, E. L., 2,578,191, Storage Battery Terminal

Mudge, W. A., 2,578,197, Thermostatic Device

Cohn, C. C., 2,578,400, Method for Providing Oxide Coating on Aluminum and Its Alloys

Ditz, C. H., and Hussey, H. A., 2,578,518, Molding Composition for Battery Containers

Giles, J. D., and Scott, R. J., 2,578,534, Separator for Electric Storage Batteries

December 18, 1951

Strickland, H. A. Jr., 2,578,760, Electric Furnace and Stock Feeding Means Therefor

Renzoni, L. S., 2,578,839, Nickel Liberator Cell

Orlik, H. G., 2,578,898, Electrolytic Removal of Metallic Coatings from Various Base Metals

Rigby, F. L., 2,578,946, Acid Hydrolysis of Proteins

Cook, W. J., and Tuck, J. H., 2,578,968, Starting Sheet for Electrolytic Separation of Nickel

Sachs, C. C., and Bond, J., 2,579,095, Photopolymerization Process and Photopolymerizable Compositions of Matter

Hubbard, D. O., 2,579,234, Vacuum Seal for Fluorine Generation System

Reid, A. F., 2,579,243, Method for the Production of Radioactive Isotopes

Brennan, R. M., 2,579,250, Electrolytic Condenser for Use on Alternating-Current Devices

White, W. C., 2,579,352, Method and Apparatus for the Quantitative Measurement of Impurities in an Atmosphere

December 25, 1951

Eckman, H. A., and Maack, H. W., 2,579,452, Malleable Iron with Boron and Bismuth

Zadra, J. B., 2,579,531, Process for Extracting Gold and Silver

Corsini, N., 2,579,551, Electrolytic Process and Apparatus for Making Copper Dust

Ebert, T. E., 2,579,557, Counter Electrode of Selenium Rectifiers

Lehmberg, W. H., 2,579,589, Storage Battery Separator

Weisberg, L., 2,579,636, Electrodeposition of Nickel

Kurlandsky, S., 2,579,743, Dry Cell and Electrode Therefor

Upper, J. A., 2,579,885, Pouring Arc Furnace

Butler, K. H., 2,579,900, Improved Calcium Halo-Phosphate Phosphor

Zinn, W. H., 2,579,994, Neutron Density Indicator Device

Gier, J. T., Boelter, L. M. K., and Bromberg, R., and Dempster, E. R., 2,580,293, Thermopile Radiometer

January 1, 1952

Ellis, G. B., 2,580,415, Primary Cell Structure

Diley, J. I., 2,580,530, Battery Sump

EMPLOYMENT SITUATION

Please address replies to box shown, c/o The Electrochemical Society, Inc., 235 W. 102nd St., New York 25, N. Y.

Position Available

CHEMICAL ENGINEER OR CHEMIST. Recent graduate for research and development work by leader in metals industry. Training in metallic coatings and electroplating desirable, but not necessary. *Reply to Box A-236.*

Editorial

Rare Metals from a Producer's Point of View

This title is both indefinite and a challenge—indefinite because "rare" has several meanings; a challenge because it may merely signify neglect. Nor is it easy to draw a sharp line between metals and nonmetals. Perhaps the most useful tool in a research laboratory is the chart of the periodic system of the elements generally found hanging on the wall. Those metals found tagged by custom as "rare," and to a lesser degree as "precious," seldom get much consideration for reasons that are psychological.

The first handicap to be overcome is the impression that "rare" connotes scarcity. What is the use of developing something if there is only a limited quantity of the element available at a probably prohibitive price? Right there we have to leave the laboratory and investigate why the element with the particular property desired is scarce. How quickly germanium dusted itself off when the transistor demand arose! An uncommon metal may be anything but scarce in nature—titanium, for instance. Here undeveloped metallurgy was the barrier in the road which the present demand is rapidly demolishing, and the price will undoubtedly continue dropping as tonnage rises.

Prices do not mean much when they are based upon beggarly tonnages. Indium can certainly be classed as a rare metal. It is currently quoted on an ounce basis, but if a firm demand developed for a tonnage which would justify zinc producers in making the necessary capital expenditures to change flow sheets in order to recover indium now lost, major price reductions would follow. The laboratory should therefore investigate the reason for any apparent scarcity.

On the other side of the picture the technical staff of a metallurgical company should not rest until a complete market is established for all the recoverable constituents of its ore. The discovery of uses for the neglected elements is a fascinating and sometimes quite simple operation. The problem is to bring the possible producer and the possible consumer to a mutual understanding of the joint opportunity.

First it is necessary to form a clear view of the commercial picture. How large is the ultimate source of the substance at your command? How much competitive production would spring up? Price will generally be found secondary to tonnage and a matter for later adjustment. No prospective consumer wants to waste time on a new product without reasonable assurance that a commensurate tonnage will be available.

Next all known information on the chemical and physical properties of the material in question should be assembled, filling in any serious gaps experimentally if necessary and including alloys when indicated—bismuth found itself in alloys and

indium is rapidly doing so. Also be sure to deal with high purity material. Mere traces of certain impurities in zinc will make it soluble in sulfuric acid. Impurities in gallium cause it to wet glass. Having obtained data on the properties of a rare metal, it is important that these be scanned for unusual characteristics. In the case of, let us say, gallium the very low melting point (30°C) as compared with the high boiling point (2070°C) stands out. This property of gallium suggests its use in place of mercury in various switching and rectifying devices.

Armed with this information you are now ready to visit all kinds of plants, offering free samples in any reasonable quantity plus all available information and with no patent blockade. The result will generally be more responsive interest than was thought possible, your only cost is that of distributing samples of a hitherto unsalable product and the other fellow pays the expenses of the tests in his laboratory on his own probably secret application. Each success will breed a dozen others.

Returning to the main thesis, the next handicap is the traditional use tag on many substances. Arsenic is apt to be thought of only as a poison, gold as jewelry, thallium as a rodenticide, bismuth as a drug. Coupled with this is the slothful resistance domiciled in many of us to new ideas. Years ago aluminum had to contend with all these barriers in the course of the change from a laboratory curiosity to a major metal. To be sure these are mainly psychological but they exist in a laboratory as well as everywhere else.

Finally there is the fairly close duplication of some of the properties of one metal by those of a brother of less cost. Cobalt has always had to contend with nickel, cadmium with zinc, and so on. Here again is where the exceptional property has to be recognized and seized upon.

The moral of all this is that the rare metal, alias neglected element, needs a sponsor as much as does a radio program. Perhaps the best of the meanings that could be given to "rare" is "unfamiliar." Take a list of the elements and read off some of those with names like a Pullman car and see how many of your friends can tell without reflection which are even metals!

Many of the rare metals concentrate in the dusts, fume, and slimes of electrochemical processes and The Electrochemical Society is not only a suitable forum but perhaps a vitalizer in the discussion of what has been largely a neglected field Papers dealing with the occurrence, properties, processes for recovery, or even imaginative use, of the neglected elements should be encouraged by the Society. The field is ours.

—Lawrence Addicks

Fiftieth Anniversary

RARE METALS AND THE ELECTROCHEMICAL SOCIETY

*Martin F. Quaely**

When The Electrochemical Society was founded in 1902 its object was recorded as being the "advancement of the theory and practice of Electrochemistry." No sections or divisions were to be established for some years. Nowhere was there any mention made of "rare" metals nor was the term electronics in use; for, at that time, the great science which was to be known as electronics was only being born, and the foundations for it were being established. With electronics there was to come the urgent call for new metals of very high purity, which had special properties of thermionic emission and were able to withstand high operating temperatures.

The Electrochemical Society did not await the maturity of electronics before it fostered discussions and publications on the "rare" metals. The history of rare metals and the history of the Society have advanced together. The history of the rare metals, however, is somewhat difficult to chronicle, inasmuch as many of the elements included in the category of rare metals are not truly rare in occurrence; rather, methods of recovery and commercial applications have not been fully developed. Furthermore, many of the elements have graduated from the class of rare metals during the life of the Society. Classical examples are aluminum and magnesium, the production of which now amounts to millions of pounds per year. Thus, we are facing a constantly changing picture wherein the rare metals of today are the commercial metals of tomorrow.

Although Hall developed his process for making aluminum in 1886, this metal was still considered rare at the turn of the century, and there were very few who had seen any pure aluminum. At the first meeting of the Society in Philadelphia in April, 1902, Burgess presented the first paper (1) on the rare metals, in which he described the use of aluminum in electrolytic rectifiers.

In 1903, the Society was given the opportunity to foster research in the rare metals when A. B. Frenzel of Denver, Colorado, "offered the sum of two hundred and fifty dollars as a prize to the member of this Society presenting the best paper embodying his research on practical methods of treating the rare minerals found in America, and extracting the rare metals therefrom. . . ." Mr. Frenzel also "offered to furnish free, for research purposes, any reasonable quantity of such ores as were at his disposal, such as ores of uranium, vanadium, molybdenum and tungsten." The Board of Directors of the Society accepted the offer with thanks. The prize remained unclaimed for several years.

At the New York meeting of 1903, Hammer gave an illustrated lecture on radium and other radioactive substances, and on the properties and applications of selenium. This lecture also included a discussion of phosphorescent and fluorescent substances.

One of the first lectures and demonstrations to be given in this country on the aluminothermic process for the production of chromium, manganese, and molybdenum was presented by Hans Goldschmidt at the St. Louis Exposition meeting in 1904. The important "Thermit" process had its origin in the early experiments of Dr. Goldschmidt.

Through the years, a large number of papers have appeared on the subject of chromium plating. Carveth and Curry (2) at the Boston meeting in 1905 reviewed previous attempts at plating chromium and gave results of their experiments. Some slight success was reported. Also, at the same meeting, Tone (3) described the practical preparation of "amorphous" silicon by the reduction of silica with carbon in the electric furnace. This paper was a starting point for additional papers on the use of the electric furnace for the preparation of metals and metalloids.

With the introduction of the incandescent lamp about 1879–80, there soon arose the problem of finding a substitute for the carbon filaments. These were gradually replaced by osmium and tantalum. The subject was reviewed by Vice-President Roeber (4) at the Bethlehem, Pennsylvania, meeting of 1905. He presented a short discussion on the thermodynamics of the incandescent lamp, pointing out the weaknesses of the carbon filament, the use of osmium in von Welsbach's lamp and of tantalum in the lamp of von Bolton. Von Bolton tried filaments of vanadium, niobium, and tantalum. The tantalum, which proved most useful, was prepared in one of two ways: (*a*) filaments were formed of brown tantalum tetroxide; with the filaments in a vacuum, an electric current was passed through them so that there was decomposition of the oxide and fusion or sintering of the metal; after heating thus for some time, a ductile wire was obtained; (*b*) potassium tantalum fluoride (K_2TaF_7) was reduced with potassium to form impure tantalum, which was purified further by heating in vacuum.

At the Ithaca meeting in May, 1906, the Board of Directors of the Society was able to announce that the Frenzel Prize of two hundred and fifty dollars was awarded to Gustave Gin of Paris, France. At the same meeting several papers were presented on molybdenum, and one on electrolytic chromium. Watts (5) showed the possible existence of a silicide having the formula $MoSi_2$. This compound has recently found an important use as a protective coating for molybdenum. Brown (6) reduced molybdenite with a mixture of lime and carbon to produce a molybdenum metal which was very brittle. In fact, the metal contained only 93.8 per cent molybdenum, the chief impurity being iron.

As translated from the French by Richards and Landis the first part of the Frenzel Prize essay by Gin was offered at the New York meeting of 1907. This first part contained a discussion of the occurrence of molybdenum in its various ores, followed by the recovery of the metal through the

* Research Dept., Westinghouse Electric Corporation, Bloomfield, New Jersey.

various stages of treatment; concentration of the ore and chemical purification of the concentrates combined with roasting to yield a purified molybdic oxide. In all, a total of ten methods for the recovery of molybdic acid were discussed. Gin also gave a number of processes for preparing molybdenum metal and alloys including hydrogen reduction of

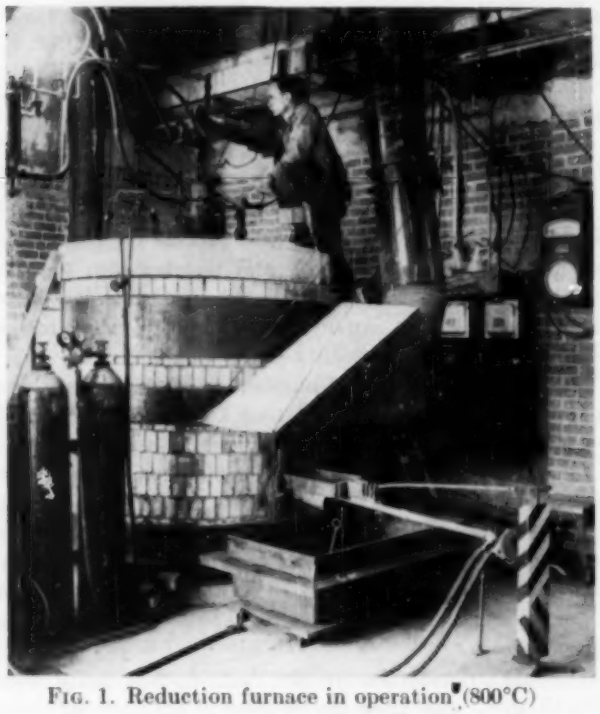

FIG. 1. Reduction furnace in operation (800°C)

FIG. 1–3 show apparatus for production of titanium developed by U. S. Bureau of Mines. Titanium tetrachloride is produced by heating the ore with carbon in chlorine. The tetrachloride is reduced in sealed containers with magnesium, and the spongy metal so obtained is sintered and finally forged or rolled into desired shapes.

the oxide, aluminum reduction of the oxide, hydrogen reduction of the chloride, and electrolysis of a fused salt mixture of the chlorides of sodium and molybdenum. Gin completed the picture with a schedule of methods for the analysis of molybdenum, its ores, and compounds.

The second part of Gin's memoir, wherein he covered the preparation of tungsten from its ores, was published in 1908. Various compounds of tungsten, such as carbide, boride, and silicide, and combinations of tungsten with the metals aluminum, nickel, iron, manganese, chromium, molybdenum, lead, and copper were discussed. Five processes for the recovery of tungsten were evaluated. The danger in predicting the success or failure of a particular process, however, is indicated by Gin's error in relegating the hydrogen reduction of the oxide to the realm of laboratory curiosities. This process is the only one that has much commercial significance today. As with molybdenum, this paper on tungsten was completed with a review of its analytical chemistry.

In addition to his memoir on the recovery of the rare metals, Gin offered a number of other papers before the meetings of the Society. At Niagara Falls, Canada, in 1909, he discussed the preparation of ferro-vanadium by electrolysis and the manufacture of silico-vanadium. At the same meeting, the physical properties of crystalline silicon were given by Zimmerman (7).

In the first few years only a couple of papers were given annually before the Society on subjects relating to the rare metals. In the year 1909 this situation changed, howeve when a total of eight papers was published. Edgar Fah Smith described the rapid electrolytic determination of ura nium, tungsten, and molybdenum, among other metal Although the use of tungsten as an incandescent lamp fil ment was introduced about 1904, the search for more suit able filament metals went on. Among the materials tried w boron, to which Weintraub (8) referred as follows: "Boro belongs at present, together with a number of other element such as zirconium, uranium, etc., to the class of practicall unknown elements." After experimenting with various known methods, Weintraub succeeded in producing fairly pure boro by reduction of boron chloride with hydrogen in an alte nating current arc with copper electrodes.

Frary and his colleagues (9), and also Johnson (10), re ported the electrolytic preparation of calcium metal in series of papers.

From time to time a paper was presented before the So ciety on radioactive materials. Schlundt and Moore, in 190 described methods of separating the radioactive component of thorium (11). A little later Johnson (12) reviewed th electrochemistry of polonium.

The third part of the memoir of Gin on the preparation the rare metals was published in 1909 on vanadium. Appar ently, the methods available for preparing the metal wer limited as he considered only the reduction of the tetra chloride with hydrogen. Gin did not, however, prepar vanadium, but alloys, mainly ferrous. The paper was con cluded with a presentation of the analytical chemistry vanadium.

Tungsten filament lamps had now become available and while the light output was much higher and a longer useful life could be expected, the industry was still faced with the problem of brittle filaments. Fink and his coworkers attacke

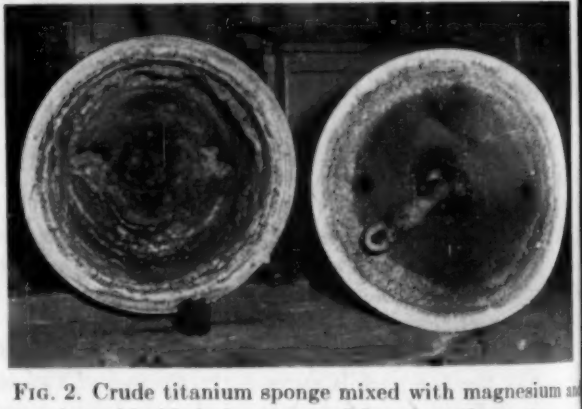

FIG. 2. Crude titanium sponge mixed with magnesium an magnesium chloride before removal from reaction pot.

this problem, and finally developed ductile tungsten as well as ductile molybdenum (13, 14). Ductile tungsten or ductile molybdenum were used by Winne and Dantsizen (15) for furnace heating elements.

At Toronto, in 1911, Hirsch (16) read a paper on the preparation and properties of metallic cerium which was then coming into extensive use. The preparation of the metal was attempted by thermal reduction of cerium compounds, which was not particularly successful. However, the electrolysis of the anhydrous fluorides and the anhydrous chlorides gave better results. The cerium could be purified by the formation of the amalgam to eliminate impurities. The physical and chemical properties of the metal were recounted.

The Board of Directors of the Society found it advisable in 1913 to appoint various sectional committees to foster

terest in the work of the Society in the respective fields. While no committees were appointed directly on electronics r rare metals, these fields of endeavor were believed to be within the scope of the appointed committees.

The years 1914–16 were a period of hard times for most people and also for the Society. Only two papers on rare metals were presented in this period. Hillebrand (17) discussed gallium and later in the year Fischer presented a comprehensive essay (18) on the electrolysis of aqueous solutions of vanadium salts. This was an extensive piece of work, and still remains the most complete exposition on the subject. As only negative results were obtained, Fischer reported: "It is obvious that with the element vanadium one is not likely to obtain the metal as cathode deposit from aqueous solutions, due to the high heats of formation of the salts and to the great tendency shown by this element to form vanadates." And to this day, nobody has yet succeeded in obtaining vanadium metal by electrolysis of aqueous solutions.

Toward the end of World War I interest in radium and radioactive materials was on the increase and the publications of the Society reflected this. The use of radium in warfare was described by Viol and Kammer (19) in 1917. Underwood and Schlundt (20) described an apparatus for separating and determining radium emanation, while Lind (21) discussed the heterogeneous equilibrium of hydrogen and oxygen mixed with radium emanation.

At the time of the presentation of the first three sections of the memoirs of Gin, a short communication on uranium was received with the statement that it would be followed by a longer dissertation on uranium, corresponding to those on molybdenum, tungsten, and vanadium. However, nothing further was received, and due to the increasing interest in uranium the short communication was published in 1919 (22). In discussing this paper Lind offered the following comments: "The postponed publication of Mr. Gin's paper at the present time lends to it an added interest in affording an opportunity of looking backward at the rapid changes that have taken place during the past ten years in the metallurgy of the rare metals . . . and any process for uranium which does not lend itself to the recovery of radium must be discarded. Uranium is not only at present a by-product, but one that must struggle hard to find a commercial outlet; only a small portion of the uranium being produced in the radium industry is finding a market at the present time." What a change in demand has occurred since that time!

In the latter years of the war there also appeared several other papers connected with rare metals. These were on the electrolytic behavior of tungsten (23), the preparation of pure alloys for magnetic purposes (24), including the preparation of pure iron, and on the role played by silicon and titanium tetrachlorides during the war (25).

During World War I, high frequency induction heating as a means of preparing pure metals proved itself a successful contender for recognition in the field of metallurgy. In order to expand the knowledge of this relatively new tool Northrup presented two papers before meetings of the Society, one on the principles of inductive heating (26), and one on advancements in inductive heating at high frequencies (27).

In the spring of 1920 at the Boston meeting, a series of seven papers was presented and this might be considered the first organized symposium on rare metals, although it was not labeled as such. Papers were offered on ferro-vanadium (28), ferro-cerium (29), electrical resistance alloys (nichrome) (30), electrolytic calcium (31), electrolytic chromium (32), stellite (33), and electrical properties of titanium alloys (34).

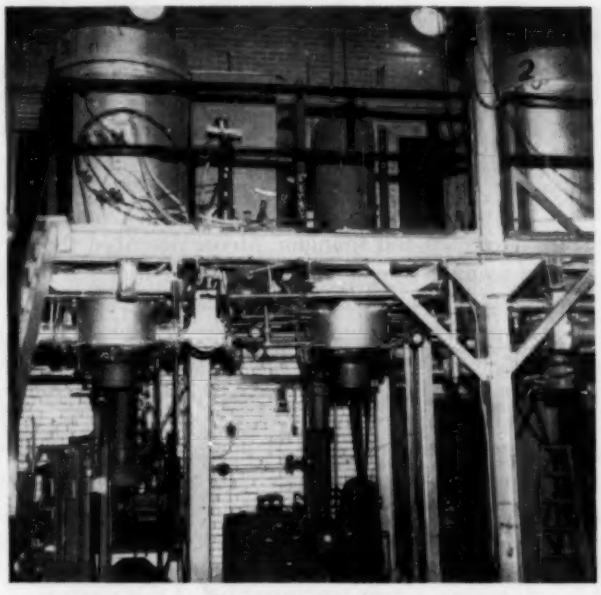

FIG. 3. Vacuum furnace for distillation of magnesium and magnesium chloride from titanium sponge.

In 1921 it was recognized that the interests of the Society could be better served by forming divisions of the Society. The constitution of the Society was amended so that "Professional groups, to be known as Divisions of the Society and to be organized from its members, may be authorized by the Board of Directors." The first divisions of the Society to be formed were those on Electrothermics and Electrodeposition. Many of the early papers relating to the rare metals were presented under their auspices.

The first formal symposium, an interesting and comprehensive session on the "Production and Applications of the Rarer Metals," was arranged by Becket for the New York meeting in 1923. It is interesting to recall some of the comments made by James in his keynote address (35): "Some metals may have been neglected either because they were considered to be absolutely useless, or because they appeared to be too rare. When an element is condemned as being useless, it is evident that its characteristic properties are deeply hidden . . . we find that in many cases good methods of separation and recovery are completely lacking. The separation of tantalum and columbium is such a case. It is highly probable that in all difficult tasks, the worker, at times, is liable to become discouraged. However, we have many fine illustra-

FIG. 4. Main floor view of U. S. Bureau of Mines zirconium production plant.

tions in the past where the problems seemed hopeless, but where the work was finally crowned with success."

Among the papers that were presented at the symposium which drew considerable discussion were those on fuzed zirconium (36) and uranium (37). Cooper treated zirconium carbide with chlorine to yield zirconium tetrachloride, which in turn was treated with sodium metal to give zirconium. This is basically the same method now used to commercially produce zirconium and titanium. Moore described the preparation of uranium wherein uranium tetrachloride was formed by treating U_3O_8 with sulfur monochloride. The UCl_4 was then reduced with sodium to produce uranium metal. In another paper, experiments on the use of the elements, uranium, boron, titanium, zirconium, cerium, and molybdenum, as alloying additions in steel were disclosed. However, in the light of present-day evidence it appears that conclusions drawn from these experiments may be somewhat erroneous, especially when the author reports that both boron and cerium are harmful in steel. Also included in the symposium were three communications on the platinum metals. In all, a total of fourteen papers was presented at this meeting.

The spring meeting of 1924 at Philadelphia produced only three papers on the rare metals. Two of these were on electrolytic production and metallurgy of beryllium by Hopkins and coworkers (38, 39), the first papers on the subject before the Society. Further attempts to electroplate tungsten were described by Mann and Halvorsen (40). During the same year two more papers appeared, one on fused salt electrolysis methods for the preparation of tungsten (41), and the other on stainless chromium steels by Hatfield (42). Stainless steels were just coming into everyday use, and it was rather fortunate for the Society to be able to hear from the originator of one of the types of stainless steel.

Another session relating to rare metals, but held under the topic of "Fused Electrolytes," was conducted at Niagara Falls, New York, in the spring of 1925. Seven papers of particular interest were given. The data on aluminum were brought up to date in papers by Frary (43), and Edwards (44). Other papers were on boron, cerium, neodymium, beryllium, and zirconium.

During the next few years, almost every meeting seemed to produce a paper or two. At Philadelphia in 1927, there were three papers on tungsten and molybdenum, concerning chiefly the preparation of pure oxides from the ores and their reduction to metal by hydrogen. These were followed in time by papers presented on thallium, beryllium, cerium, columbium, tantalum, germanium, and indium.

During the twenties the number of papers on rare metals and related subjects was on the increase, and this more or less necessitated the formation of committees to guide the work. In 1930, a Technical Committee on Electronics was formed with Herman Schlundt as chairman, and O. H. Caldwell as member. This led to the establishment of the Electronics Division. Upon the recommendation of President Kahlenberg of the Society, the Board of Directors approved of the formation of this new section at the Birmingham meeting in April 1931. Professor Schlundt was elected first chairman of the new Electronics Division with O. H. Caldwell and J. A. Becker as members. At this meeting several papers appeared on the electrodeposition of rare metals (45–47).

The increasing interest in the rare metals during the early thirties is reflected in the increased volume and diversity of topics published. Stock's (48) paper in 1932 on beryllium was a forerunner of others on the same metal in later years. He produced beryllium by fused salt electrolysis from a melt which was started with $NaBeF_3$ and continued by addition of $BaBe_2F_6$. Molybdenum, titanium, germanium, indium, rhodium, tantalum, and columbium were also subjects for discussion at various meetings of the Society in this period.

At the spring meeting of 1934 in Asheville, North Carolina, Hall and Koenig (49) described the electrochemical properties of germanium; Calhane and Laliberte (50) explained the electrolytic valve action of columbium and tantalum on a-c circuits; and Gray (51) discussed the electrodeposition of indium.

After a period of nearly twelve years, the fall of 1934 found the Society meeting once again in New York City. The main session consisted of a symposium on the "Electrochemistry of the Rarer Elements." The minutes of the meeting noted that the most important strides had been made in the field of rare elements in the years that had elapsed since the previous New York meeting. It was further recorded: "The valuable alloying properties of beryllium and lithium have been commercially established.—Barium has usurped thorium's dominating position as an electron emitter and 'getter.' Germanium has become a 'forced' by-product of the electrolytic zinc industry. Bismuth is no longer primarily of pharmaceutical interest, but has found many new metallurgical uses. Columbium has invaded the steel plant.—Tungsten, as carbide, has displaced diamonds for drills, dies, etc." In these intervening years the discovery of six additional elements was also disclosed.

At that meeting, papers were presented on the following subjects: titanium in metallurgy (52), vanadium (53), thorium and uranium (54), europium (55), cerium group metals (56), calcium (57), nickel-barium alloys (58), lithium (59), gallium (60), boron carbide (61), electrolysis of nonaqueous solutions of rare earth metal salts (62), beryllium (63), deposition of tungsten-iron alloys (64), tungsten (65), and rhenium plating (66).

In 1936, at Cincinnati, there were papers tracing the development of columbium from a curiosity to a full-scale commerical product (67), and also, on the rare earth metals (68).

During the late thirties the rarer metals were becoming less and less laboratory curiosities. Many of the metals could be obtained in a high state of purity, and the papers which were presented before the Society in this period were concerned chiefly with the properties and applications of the metals.

For the Ottawa meeting of 1940, there was a session on "Electronics and Electrothermics." Of special importance, in the light of later developments, was the presentation of a paper on the production of ductile titanium by Kroll (69) who prepared the metal by reducing $TiCl_4$ with pure magnesium in a molybdenum-lined crucible, in the presence of pure argon, at a temperature of about 1000°C. By leaching and acid treatment, the titanium was separated from impurities. The powdered metal was compressed and sintered in vacuum. During the preparation and handling it was of prime importance to avoid contamination with oxygen or nitrogen. That it was feasible to produce a ductile metal in quantity was readily shown, and later developments in this direction have stemmed from the researches conducted by Kroll and his colleagues.

During World War II, the activities of the Society were somewhat curtailed. Many new developments were classified as secret. The majority of the papers on rare metals that were published were concerned with the electrodeposition of the metals or of their alloys.

As it was the policy of the Society that each division be guided by a code of bylaws, it became necessary for the Electronics Division to draw up such a code. After having been passed upon by the Policy Committee of the Society, the bylaws were accepted by the Board of Directors on July 24, 1942.

At the meetings held in 1943–44 a number of papers of considerable importance appeared. With his continuing interest in tungsten, Fink (70) described the preparation of pure tungsten direct from ore by electrolysis from fused borax and fused phosphate baths. During the war the airplane engine manufacturers were interested in obtaining better bearing materials. Several of our members made valuable contributions in solving the problem, and the diffused lead-indium bearing resulted through their research. Two timely papers were presented on indium, one with direct reference to the lead-indium alloys (71). The other (72) pertained to the recovery of indium from lead-tin alloys. Balke (73) disclosed a method for preparing pure columbium oxide and columbium carbide. A ductile metal is eventually obtained.

Although the meetings scheduled for 1945 were cancelled on account of the war, it was possible to hold several regional meetings, at which a number of important papers were presented (74–79).

After the war the regular meetings of the Society were resumed. The first was in the spring of 1946 at Birmingham, where another symposium on the rare metals was held. Ten papers were presented, three of which dealt with beryllium (80). Dr. James' comments in 1923 on beryllium, and the difficulties in recovering this metal, are most interesting at this point; 23 years later, the three papers at the symposium showed that beryllium was now in commercial production for many important uses. Similar examples could be cited for other elements. The release from wartime restriction was evident from the subject matter presented at the symposium. In addition to beryllium, other topics for discussion included the production of calcium (81), the working of molybdenum (82), ductile zirconium (83), scandium (84), uranium and radium (85), the electrochemistry of the rare earth group (86), and germanium (91). In connection with the symposium, a "Rare Metals Exhibit" was held in which there were displayed samples of germanium, zirconium, and beryllium. At succeeding meetings of the Society the rare metals were the subjects of discussion many times. Although no formal session on rare metals was held during 1947, the Electronics Division did sponsor a session on "Electronics" at Louisville, where several papers concerned with the rare metals were presented. These were on cobalt (87), zirconium (88), and tantalum (89). A paper also appeared in the same year on malleable zirconium (90).

The next Symposium on Rare Metals took place at the Columbus meeting of April, 1948. Twelve papers were presented, and the interest was so great that, at the annual business meeting of the Electronics Division, it was decided to form a Rare Metals Group within the Division, and to sponsor yearly symposia on the Rare Metals. The Columbus symposium, especially, was of value because there were so many papers on the production of the rare metals themselves. A number were also presented at the fall meeting in New York (92–97).

The next Symposium on Rare Metals was assembled at Philadelphia in May, 1949. The increasing importance of the rare elements was shown by the large number of papers that were presented. Another annual Symposium on the Rare Metals was held at Cleveland in April, 1950. In all, 31 papers were presented. Especially worthy of note was the series of papers on vanadium, the first on the metal itself before the Society since Gin's memoir appeared in 1909.

The next Symposium on Rare Metals was at the 1951 spring meeting in Washington. Three sessions were held, one a joint session with the Electrothermics Division. Of the 18 papers presented, five concerned molybdenum, an indication of the importance being attached to this metal. In fact, the subject matter of the papers presented at the recent symposia shows that at the present time, research efforts are being directed toward the preparation of metals for use at high temperatures under high stresses, for atomic energy purposes, and for special uses, such as the germanium transistor elements in communications equipment.

With the introduction of the JOURNAL of the Society, the publication of the monthly *Bulletin* of the Society was suspended permanently. From 1943–47 this bulletin served as a quick reference on rare metals, for a feature of each issue was an article of a page or so on one of the rare metals by Dr. Fink. Twenty-seven elements were covered in this series of articles.

In the one-hundred meetings of the Society there have been presented approximately 330 papers relating to the rare metals, distributed as follows: tungsten 32, zirconium 26, molybdenum 25, titanium 23, chromium 20, beryllium 17, vanadium 14, germanium 12, tantalum 12, boron 9, indium 9, columbium 9, calcium 8, cobalt 8, uranium 8, cerium 7, platinum 7, radium 6, aluminum 5, silicon 5, rhenium 5, thorium 4, gallium 3, lithium 3, 2 each on barium, selenium, polonium, thallium, palladium, rhodium, and tellurium, and 49 on other metals and related subjects.

In looking back over the past fifty years and with consideration of the prediction made about a few of the elements which have since found important applications (although not always along the same lines as were predicted), one gathers the impression that all of the newer "rare" elements will eventually find their own niches in our science and economy.

REFERENCES

All papers listed in the References below appeared in the TRANSACTIONS or the JOURNAL of The Electrochemical Society.

1. C. F. BURGESS AND CARL HAMBUECHEN, "The Electrolytic Rectifier," **1**, 147 (1902).
2. H. R. CARVETH AND B. E. CURRY, "Chromium and the Electrolysis of Chromic Acid," **7**, 115 (1905).
3. F. J. TONE, "Production of Silicon in the Electric Furnace," **7**, 243 (1905).
4. E. F. ROEBER, "Thermodynamics of the Incandescent Lamp," **8**, 243 (1905).
5. O. P. WATTS, "A New Silicide of Molybdenum," **9**, 105 (1906).
6. O. W. BROWN, "The Reduction of Metal Sulfides," **9**, 109 (1906).
7. C. I. ZIMMERMAN, "Some Physical Properties of Crystalline Silicon," **15**, 395 (1909).
8. E. WEINTRAUB, "Preparation and Properties of Pure Boron," **16**, 165 (1909).
9. F. W. FRARY AND W. L. BADGER, "The Preparation of Calcium," **16**, 185 (1909).
   F. W. FRARY, H. R. BICKNELL, AND C. A. TRONSON, "Efficiency in the Electrolytic Production of Metallic Calcium," **18**, 117 (1910).
10. A. R. JOHNSON, "The Electrolytic Preparation of Calcium," **18**, 125 (1910).
11. H. SCHLUNDT AND R. B. MOORE, "On the Chemical Separation of the Excited Activity of Thorium," **8**, 269 (1905).

12. A. R. Johnson, "Electrochemistry of Polonium and Other Radioactive Elements," **18,** 165 (1910).
13. C. G. Fink, "Ductile Tungsten and Molybdenum" **17,** 229 (1910).
14. C. G. Fink, "Applications of Ductile Tungsten," **22,** 499 (1912).
15. R. Winne and C. Dantsizen, "Small Electric Furnace with Heating Element of Ductile Tungsten or Ductile Molybdenum," **20,** 287 (1911).
16. A. Hirsch, "The Preparation and Properties of Metallic Cerium," **20,** 57 (1911).
17. W. F. Hillebrand, "Gallium," **29,** 8 (1916).
18. S. Fischer, Jr., "Contributions to the Knowledge of the Electrolysis of Aqueous Solutions of Vanadium Salts," **30,** 175 (1916).
19. C. H. Viol and G. D. Kammer, "The Application of Radium in Warfare," **32,** 381 (1917).
20. J. E. Underwood and H. Schlundt, "An Apparatus for the Separation of Radium Emanation and Its Determination Electroscopically," **34,** 203 (1918).
21. S. C. Lind, "Notes on the Heterogeneous Equilibrium of Hydrogen and Oxygen Mixed with Radium Emanation," **34,** 211 (1918).
22. G. Gin, "Uranium: Its Extraction from Pitchblende," **35,** 191 (1919).
23. W. E. Koerner, "The Electrolytic Behavior of Tungsten," **31,** 221 (1917).
24. T. D. Yensen, "Preparation of Pure Alloys for Magnetic Purposes," **32,** 165 (1917).
25. G. A. Richter, "The Role Played by Silicon and Titanium Tetrachlorides During the Past War," **35,** 323 (1919).
26. E. F. Northrup, "Principles of Inductive Heating with High Frequency Currents," **35,** 69 (1919).
27. E. F. Northrup, "Recent Progress in High Frequency Inductive Heating," **39,** 331 (1921).
28. B. D. Saklatwalla, "Development of Ferro-Vanadium Metallurgy," **37,** 341 (1920).
29. A. Hirsch, "Ferrocerium," **37,** 359 (1920).
30. R. M. Major, "The Electrical Production of Alloys," **37,** 457 (1920).
31. P. H. Brace, "The Electrolytic Production of Calcium," **37,** 465 (1920).
32. G. J. Sargent, "Electrolytic Chromium," **37,** 479 (1920).
33. E. Haynes, "Stellite," **37,** 507 (1920).
34. M. A. Hunter and J. W. Bacon, "Some Electrical Properties of Titanium Alloys," **37,** 513 (1920).
35. C. James, "Present Status of the Production of Rarer Metals," **43,** 203 (1923).
36. H. S. Cooper, "The Preparation of Fused Zirconium," **43,** 215 (1923).
37. R. W. Moore, "Preparation of Metallic Uranium," **43,** 317 (1923).
38. B. S. Hopkins and A. W. Meyer, "The Electrolytic Production of Beryllium," **45,** 475 (1924).
39. E. A. Engle and B. S. Hopkins, "The Metallurgy and Alloys of Beryllium," **45,** 493 (1924).
40. C. A. Mann and H. O. Halvorsen, "An Attempt to Electroplate Tungsten on Iron," **45,** 493 (1924).
41. L. Kahlenberg and H. H. Kahlenberg, "The Preparation of Metallic Tungsten and some of Its Alloys," **46,** 181 (1924).
42. W. H. Hatfield, "The 'Stainless' Chromium Steels," **46,** 297 (1924).
43. F. C. Frary, "The Electrolytic Refining of Aluminum," **47,** 275 (1925).
44. J. D. Edwards, "The Properties of Pure Aluminum," **47,** 287 (1925).
45. C. G. Fink and F. L. Jones, "The Electrodeposition of Tungsten from Aqueous Solutions," **59,** 461 (1931).
46. W. Keitel and H. E. Zschiegner, "Electrodeposition of Platinum, Palladium, and Rhodium," **59,** 273 (1931).
47. K. Sasaki and S. Sekito, "Three Crystalline Modifications of Electrolytic Chromium," **59,** 437 (1931).
48. A. Stock, "Beryllium," **61,** 255 (1932).
49. J. I. Hall and A. E. Koenig, "Electrochemical Properties of Germanium," **65,** 215 (1934).
50. D. F. Calhane and A. J. Laliberte, "The Electrolytic Valve Action of Columbium and Tantalum on A.C. Circuits," **65,** 291 (1934).
51. D. Gray, "The Electrodeposition of Indium from Cyanide Solutions," **65,** 377 (1934).
52. M. A. Hunter and A. Jones, "Titanium in Metallurgy," **66,** 21 (1934).
53. B. D. Saklatwalla, "Vanadium," **66,** 33 (1934).
54. J. W. Marden, "The Production and Utilization of Thorium and Uranium," **66,** 39 (1934).
55. B. S. Hopkins, "Europium, A Rare Member of the Rare Earth Group," **66,** 49 (1934).
56. F. Trombe, "The Production of Metals of the Cerium Group," **66,** 57 (1934).
57 C. L. Mantell and C. Hardy, "Calcium: Its Metallurgy and Technology," **66,** 63 (1934).
58 D. W. Randolph, "Alloys of Nickel and Barium," **66,** 85 (1934).
59 H. Osborg, "Lithium," **66,** 91 (1934).
60 H. C. Fogg, "A Review of the Electrochemistry of Gallium," **66,** 107 (1934).
61 R. R. Ridgway, "Boron Carbide. A New Crystalline Abrasive and Wear-Resisting Product," **66,** 117 (1934).
62 B. S. Hopkins and L. F. Audrieth, "The Electrolysis of Rare Earth Metal Salts in Non-Aqueous Solvents," **66,** 135 (1934).
63. F. H. Getman, "The Normal Potential of Beryllium," **66,** 143 (1934).
64. M. L. Holt, "The Co-deposition of Tungsten and Iron from Aqueous Solutions," **66,** 453 (1934).
65. Shoo-Tze Leo and Tsing-Nang Shen, "Electrolytic Production of Tungsten Metal from a Fused Phosphate Bath," **66,** 461 (1934).
66. C. G. Fink and P. Deren, "Rhenium Plating," **66,** 471 (1934).
67. J. H. Critchett, "Columbium from a Laboratory Curiosity to a Widely Used Commercial Product," **69,** 62 (1936).
68. D. W. Pearce, C. R. Naeser, and B. S. Hopkins, "Observations on the Rare Earths. Part XLII. Studies in the Electrolytic Reduction of Ytterbium," **69,** 557 (1936).
69. W. Kroll, "The Production of Ductile Titanium," **78,** 35 (1940).
70. C. G. Fink and Chuk Ching Ma, "Pure Tungsten Direct from Ore. 1. Electrolytic Tungsten from Fused Borax and Fused Phosphate Baths," **84,** 33 (1943).
71. J. M. Freund, H. B. Linford, and P. W. Schutz, "Corrosion of Lead-Indium Diffusion Alloys," **84,** 65 (1943).
72. J. Coyle, "Extraction of Indium from Complex Lead-Tin Alloys," **85,** 223 (1944).
73. C. Balke, "Pure Columbium," **85,** 89 (1944).
74. H. C. Rentschler and D. E. Henry, "Lowering of the Photoelectric Work Function of Zirconium, Titanium, Thorium and Similar Metals by Dissolved Gases," **87,** 289 (1945).
75. W. J. Kroll, "Fused Salt Electrolysis for the Production of Metal Powders," **87,** 551 (1945).
76. W. J. Kroll, "Melting and Evaporating Metals in a Vacuum," **87,** 571 (1945).
77. N. Fedotov, "Extraction of Pure Cobalt by Electrochemical Treatment of Industrial Waste," **87,** 547 (1945).
78. D. B. Alnutt and C. L. Scheer, "Zirconium Metal, Its Manufacture, Fabrication, and Properties," **88,** 195 (1945).
79. P. F. Hoglund and M. L. Holt, "Electrodeposition of Nickel-Cobalt-Tungsten Alloys from an Acid Plating Bath," **88,** 359 (1945).

H. C. Kaweck, "The Production of Beryllium Compounds, Metal and Alloys," **89**, 229 (1946).

J. M. Tien, "Preparation of Beryllium Powder," **89**, 237 (1946).

B. R. F. Kjellgren, "The Production of Beryllium Oxide and Beryllium Copper," **89**, 247 (1946).

C. C. Loomis, "The Production of Metallic Calcium by Thermal Reduction," **89**, 207 (1946).

J. W. Marden and D. M. Wroughton, "The Effect of Working on the Physical Properties of Molybdenum," **89**, 217 (1946).

W. J. Kroll, A. W. Schlechten, and L. A. Yerkes, "Ductile Zirconium from Zircon Sand," **89**, 263 (1946).

H. S. King, "Scandium in the Stars," **89**, 301 (1946).

S. C. Lind, "Uranium and Radium in the Postwar Period," **89**, 291 (1946).

B. S. Hopkins, "Electrochemistry of the Rare Earth Group," **89**, 295 (1946).

F. K. Shelton, R. E. Churchward, J. C. Stahl, and C. W. Davis, "Electrolytic Cobalt—A Commercially Feasible Process," **91**, 115 (1947).

W. C. Lilliendahl and H. C. Rentschler, "Recent Developments on the Preparation of Zirconium," **91**, 285 (1947).

W. R. Carmody, "The Electrolytic Valve Action of Zirconium," **91**, 309 (1947).

L. F. Yntema and R. W. Yancey, "Some Applications of Tantalum in Electronics," **91**, 319 (1947).

W. J. Kroll, A. W. Schlechten, W. R. Carmody, L. A. Yerkes, H. P. Holmes, and H. L. Gilbert, "Recent Progress in the Metallurgy of Malleable Zirconium," **92**, 99 (1947).

R. I. Jaffee, E. W. McMullen, and B. W. Gonser, "Technology of Germanium," **89**, 277 (1946).

W. J. Kroll, C. T. Anderson, H. P. Holmes, L. A. Yerkes, and H. L. Gilbert, "Large-Scale Laboratory Production of Ductile Zirconium," **94**, 1 (1948).

F. C. Frary, "The Electrolytic Production of Aluminum," **94**, 31 (1948).

R. R. Lloyd, J. B. Rosenbaum, V. E. Homme, and L. P. Davis, "Pilot-Plant Production of Electrolytic Chromium," **94**, 122 (1948).

P. H. Brace, "Reactions of Molten Titanium With Certain Refractory Oxides," **94**, 170 (1948).

C. G. Fink and V. M. Dokras, "Electrodeposition and Electrowinning of Germanium," **95**, 80 (1949).

L. E. Netherton and M. L. Holt, "Electrodeposition of Rhenium from Aqueous Solutions," **95**, 324 (1949).

INSTRUMENTATION AND THE GROWTH OF ELECTROCHEMISTRY

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Introduction

Electrochemistry, like most sciences, has always relied heavily upon correlation of experimental measurements. Thus the mutual impact of instrumentation and electrochemistry is a natural consequence and is obvious from a study of the publications of The Electrochemical Society during its first half-century of existence. Many of these publications deal with (*a*) the development of new instruments and primary elements, (*b*) theoretical and experimental evaluation of the characteristics and applicability of primary elements, and (*c*) the application of existing instruments to measurements of particular interest to electrochemists, electrometallugists, and electronics engineers. In the numerous publications of the Society may be found papers on almost every type of useful measurement and measuring apparatus including *p*H, electrolytic conductivity, analysis of gases, liquids and solids, coulometers and coulometric analysis, polarography, oscillography, microscopy, photography, spectrometry, radioactivity, electron and x-ray diffraction, differential thermal analysis, potentiometry, potentiostats, thermometry and pyrometry, and electronic instrumentation.

The authors have prepared a bibliography which is intended to serve as a guide for those interested in following the progress of instrumentation as it relates to activities of The Electrochemical Society. The compiling of the bibliography required a certain arbitrary selectivity in omitting some papers in which instrumental details are incomplete. This is particularly true of selections made from more recent volumes of the Society's publications. However, typical papers are included that will serve as sources for additional references.

The First Thirty Years

When the Society was founded in 1902 there were no such instruments as *p*H meters, vacuum tube voltmeters, recording potentiometers, optical or radiation pyrometers, oscilloscopes, and polarographs. Indeed, the first practical form of hydrogen gas electrode for electrometric measurement of *p*H was proposed in 1911 by Wood, Sand, and Law[1]. Thus the history of electrochemical instrumentation parallels that of The Electrochemical Society. In many instances the contents of papers and accompanying discussions display a remarkable foresight. Early contributions (prior to 1914) reflect the electrochemists' natural desire to have better coulometers and a more precise value for the Faraday constant. Yet in this same era Dr. Northrup published two papers indicative of tremendous developments to come. His paper (5) in 1909 probably led to later ideas culminating in the development of induction melting of alloys. Another of his papers (6) signaled the birth of a trend in instrumentation which has since grown into a multimillion dollar annual industry. Nor can one overlook the contribution of Foster (9) in 1910 which discloses the basic principle of operation still employed in many modern radiation pyrometers. The discussion of Ziegel's (13) paper in 1914 is truly enlightening in terms of subsequent developments in automatic titrations. It is found in a communicated discussion by Ziegel: "The author has completed his work on this phase and anticipates further applying the hydrogen electrode by causing current changes in a solution being titrated to record changes in voltage on a moving sheet of paper in such a way that the number of cc of solution required for a titration will be recorded permanently on a chart." It is interesting that these thoughts were expressed only three years after the first recorded use of a hydrogen gas electrode[1] and five years after Northrup's paper (6) on "autographic registration" of cooling curves for steel. Yet the next papers on automatic titrations appearing in the Society's publications were those of Barredo and Taylor (83) and Robinson (84) in 1947. Another prominent example of delayed follow-up is noted with reference to coulometry. Although half of the papers cited in the appended bibliography up to 1912 are on coulometers, it is only within the past ten or fifteen years that coulometric analysis and titration have received serious consideration. It is noteworthy that the Society's first scheduled symposium on coulometric methods will be held in May 1952.

The years 1915 to 1932 mark a period of comparative inactivity in instrumentation publications, apparently due to a shifting of interest and emphasis to theoretical and applied electrochemistry, electrodeposition, and electrometallurgy. Most papers on instrumentation (16, 17, 19, 20, 21) that appeared in this period were primarily devoted to measurements of acidity and alkalinity.

The Electronics Era

In 1932 the impact of electronics became evident and a new era of interest and activity in instrumentation started. Instrumentation became recognized as a separate and important technology requiring specialized attention. In 1937 the first organized instrumentation symposium of The Electrochemical Society was held in St. Louis. It dealt with "*p*H Determination and Process Control." Similar symposia have since been a regular part of the Society's activities. At the Cleveland meeting in 1950 the Electronics Division decided to hold an instrumentation symposium every two years under the sponsorship of the General Electronics group. This official recognition of the need for such symposia and the assumption of a degree of responsibility by the Electronics Division are forward steps which are not intended to divert the interest of other divisions from instrumentation.

Electronic instrumentation gave impetus to the practical application of high-impedance primary elements such as the vacuum photocell (31) and the glass electrode (37, 40). In the latter case it is significant that the glass electrode was proposed by Cremer[2] in 1906 and further developed by Haber

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[1] J. T. Wood, H. J. Sand, and D. J. Law, *J. Soc. Chem. Ind. (London)*, **30**, 871 (1911).

[2] M. Cremer, *Z. Biol.*, **47**, 562 (1906).

and Klemensiewicz[3] in 1909 but its general practical application was delayed until the era of electronic instrumentation. The invention of the cathode-ray tube provided electrochemists with a new tool for instrumental methods (45) and, with the advent of fluorescent lamps, radar, and television, a new problem to solve in the development of suitable phosphors (82, 91).

It is difficult to assess the absolute importance of modern electrochemical instrumentation as it serves industry in obtaining improved quality and uniformity at increased production levels and lower labor costs. Some idea of its importance is indicated by the dollar sales of an item such as *p*H instruments and accessories which are reported to be in excess of two million dollars for the year 1951 alone. When one realizes that this represents the growth of a single item from practically zero twenty-five years ago it conveys some idea of present-day dependence upon instrumentation.

Electronics has contributed greatly to the precise measuring and recording of electrical quantities as well as to adapting such measurements to automatic process control. Certainly one can look for continued advances in simplification of electronic instruments and broader application of electronics in instrumentation. The fields of coulometric methods, dielectric loss measurements, potentiostats, and automatic titrations are now in their infancy as electronic applications. Important future developments in these areas may be expected.

In Retrospect

The real value of history is in providing guidance for the future. A review such as this would be incomplete without an attempt to examine critically past performance. Thus, without citing specific examples, it can be said that the value of some papers might have been enhanced by more complete descriptions of the instrumentation employed. The lack of seemingly minor details not familiar to the reader is not only exasperating but detracts from the scientific value of a paper. In some instances a quantity to be measured may not justify the use of precise instruments or vice versa. It is felt that a reader is entitled to the experts' views on such matters.

One of the most gratifying aspects of the preparation of this review has been the examination of published discussions of papers. This is aptly highlighted in a portion of Kahlenberg's paper[4] presented at the twenty-fifth anniversary meeting in Philadelphia: "All of the phases of electrochemistry and its applications have been cultivated by the Society, and this has been done largely by the presentation of papers of merit which have been frankly and thoroughly discussed. In fact, it may be said that the meetings of the American Electrochemical Society have been characterized by an unusual degree of informality, cordiality, and goodwill, which has resulted in practically perfect freedom of expression of opinion and interchange of ideas, with corresponding benefits to the membership." There is food for serious thought in Dr. Kahlenberg's statement in view of the current tendency of most scientific societies to allot insufficient time per paper and consequently to eliminate the possibility of adequate discussion. In concluding this review it would be remiss not to acknowledge most valued contributions under "Discussion" made by many of our members, so well remembered and respected for their efforts.

[3] F. Haber and Z. Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

[4] Louis Kahlenberg, *Trans. Am. Electrochem. Soc.*, **51**, 41 (1927).

Electrochemical Society Symposia on Instrumentation Measurements and Control

1937 (St. Louis)—"*p*H Determination and Process Control"
1943 (Pittsburgh)—"Automatic Control of Industrial Processes"
1947 (Boston)—"Electrochemical Methods of Laboratory Control"
1950 (Cleveland)—(1). "Electronic Instrumentation"; (2). "Instrumentation in the Chlor-alkali Industry"
1951 (Washington)—"Measurements of High Temperatures"
1952 (Philadelphia)—(A). "Methods of Analysis Based upon Faraday's Law"; (B). "Modern Instruments for Chemical Analysis"

BIBLIOGRAPHY

Chronological Listing of Papers on Instrumentation and Instrumentology Published in the Transactions or Journal of The Electrochemical Society

1. Isaac Adams and Barry MacNutt, "Some Phenomena Observed in Connection with the Use of a Copper Voltameter," **5**, 191 (1904).
2. Anson G. Betts and Edward F. Kern, "The Lead Voltameter," **6**, 67 (1904).
3. K. E. Guthe, "The Silver Voltameter," **6**, 96 (1904).
4. Howard L. Bronson, "The Construction and Accurate Measurement of Resistances of the Order of One Hundred Thousand Ohms," **13**, 231 (1908).
5. Edwin F. Northrup, "A New Type of Ammeter for the Accurate Measurement of Alternating Currents above 1000 Amperes," **15**, 303 (1909).
6. Edwin F. Northrup, "Cooling Curves and a New Type of Apparatus for Their Autographic Registration," **15**, 331 (1909).
7. Charles E. Foster, "A New Radiation Pyrometer," **15**, 361 (1909).
8. J. W. Turrentine, "A Modified Oxy-Hydrogen Gas Coulometer," **15**, 515 (1909).
9. C. E. Foster, "A New Radiation Pyrometer," **17**, 223 (1910).
10. Frank C. Mathers and Albert F. O. Germann, "Mercurous Perchlorate Electrolytic Meter," **19**, 69 (1911).
11. G. D. Buckner and G. A. Hulett, "Studies on the Silver Coulometer," **22**, 367 (1912).
12. Edward W. Washburn and Stuart J. Bates, "The Iodine Coulometer and the Value of the Faraday," **22**, 397 (1912).
13. Henry Ziegel, "On Electrometric Titrations," **26**, 91 (1914).
14. Earl A. Keeler, "Industrial Applications of Electrolytic Conductivity Measurements," **38**, 113 (1920).
15. Victor F. Hess, "A New Method of Determining the Radium Content of Carnotite Ores and Other Products of Low Activity," **41**, 287 (1922).
16. N. Howell Furman, "Electrotitration with the Aid of the Air Electrode," **43**, 107 (1923).
17. William A. Mudge, "Hydrogen Ion Measurements in the Electrometallurgy of Nickel," **47**, 137 (1925).
18. H. E. Haring, "A Simple Method for Measuring Polarization and Resistivity," **49**, 417 (1926). Discussion by W. S. Smith, p. 440.
19. Henry C. Parker and Willard N. Greer, "Hydrogen Ion Control of Nickel-Plating Baths with the Quinhydrone Electrode," **49**, 451 (1926).
20. R. E. Brewer and G. H. Montillon, "Measurements of Hydrogen Ion Concentration in Plating Baths," **55**, 357 (1929).
21. Louis Kahlenberg and Albert C. Krueger, "On Simple Methods of Potentiometric Titration of Acids and Bases," **56**, 201 (1929).

22. H. A. Mangan and Herman Schlundt, "A Spinthariscope for Measuring Radioactivity," **59,** 199 (1931).
23. B. Gosman and J. Heyrovsky, "Analysis of Petroleum and its Distillates," **59,** 249 (1931).
24. J. Livingston R. Morgan, Olive M. Lammert, and Margaret A. Campbell, "The Preparation and Reproducibility of the Quinhydrone Electrode," **61,** 405 (1932).
25. Friedrich Müller, "Electromotive Force Measurements with the Aid of Electron Tubes," **62,** 335 (1932).
26. K. G. Compton and H. E. Haring, "A Compensated Thermionic Electrometer," **62,** 345 (1932).
27. W. O. Reevely and A. R. Gordon, "The Use of Micro-Coulometers in the Determination of Transport Numbers by the Moving Boundary Method," **63,** 167 (1933).
28. E. Newbery, "Metallized-glass Hydrogen Electrodes," **64,** 209 (1933).
29. E. Newbery, "Metallized-glass Quinhydrone Electrodes," **65,** 227 (1934).
30. M. deKay Thompson and Albert L. Kaye, "The Decomposition Potentials and Conductivities of Magnesium Oxide and of the Alkaline Earths in Fused Fluorides," **67,** 169 (1935).
31. E. D. Wilson, "Comparison of Photoemissive and Photovoltaic Devices. Their Use in Measuring Radiant Energy in Various Spectral Regions," **69,** 433 (1936).
32. Marlin E. Fogle, "Application of the 'Photronic' Photocell to Chemical Processes," **69,** 443 (1936).
33. Colin G. Fink and Richard C. Dehmel, "The Potential Differences at Metal-Vapor, Vapor-Liquid and Liquid-Metal Interfaces of Partially Immersed Electrodes," **70,** 281 (1936).
34. D. A. MacInnes and L. G. Longsworth, "The Measurement and Regulation of *p*H with the Glass Electrode," **71,** 73 (1937).
35. Otto H. Müller amd J. Percy Baumberger, "Oxidation-Reduction Potentials Measured with the Dropping Mercury Electrode. Part I. Studies with Quinhydrone and Estimation of Limits of Mesaurement," **71,** 169 (1937).
36. Otto H. Müller and J. Percy Baumberger, "Oxidation-Reduction Potentials Measured with the Dropping Mercury Electrode. Part II. Polarographic Investigation. An Introduction to a New Method," **71,** 181 (1937).
37. R. H. Cherry, "The Measurement of Direct Potentials Originating in Circuits of High Resistance," **72,** 33 (1937).
38. Walter J. Hamer, "Application of Halide Reference Half Cells to *p*H Determinations," **72,** 45 (1937).
39. D. I. Hitchcock, "A Standardization of the *p*H Scale," **72,** 89 (1937).
40. Malcolm Dole and B. Z. Wiener, "The Theory of the Glass Electrode. IV. Temperature Studies of the Glass Electrode Error," **72,** 107 (1937).
41. Malcolm Dole and J. L. Gabbard, "Additional Notes on the Glass Electrode. I. Glass Electrode Errors at 30°C. II. Properties of Lithium Glass Electrodes," **72,** 129 (1937).
42. T. R. Ball, "The Antimony Electrode in *p*H Measurements," **72,** 139 (1937).
43. W. N. Greer, "Industrial *p*H Control with the Antimony Electrode," **72,** 153 (1937).
44. L. O. Grondahl, "Copper Oxide Rectifiers," **72,** 225 (1937).
45. L. A. Matheson and N. Nichols, "The Cathode Ray Oscillograph Applied to the Dropping Mercury Electrode," **73,** 193 (1938).
46. J. D. Parent and C. A. Crowley, "The Differential Dynamometer as an Instrument for Conductometric Methods of Analysis. Part I. Design and Calibration," **73,** 223 (1938).
47. J. D. Parent and R. J. Melchione, "The Differential Dynamometer as an Instrument for Conductometric Methods of Analysis. Part II. Operational Characteristics, Technique, Use with Certain Reactions," **73,** 237 (1938).
48. J. S. Blair, "Use of the Glass Electrode to Evaluate Quinhydrone Electrode Errors in the Examination of Canned Foods," **74,** 567 (1938).
49. Arthur E. Lorch, "Studies of Electrochemical Polarization. The Reaction of the Hydrogen Electrode with Oxidizing Agents, and the Determination of *p*H in Their Presence," **74,** 587 (1938).
50. Julius Sendroy, Jr., "The Measurement of Blood *p*H," **74,** 595 (1938).
51. Henry H. Baker, Jr., and Ralph H. Müller, "A Pulse Amplifier for Performing Differential Electrometric Titrations," **76,** 75 (1939).
52. G. A. Perley, "The Detection of Small Traces of Copper Using the Antimony Electrodes," **76,** 85 (1939).
53. G. A. Perley, "Measurements with the Dropping Mercury Electrode," **76,** 91 (1939).
54. Elbert M. Mahla, "Stress in Electrodeposited Copper as Determined by X-Rays," **77,** 145 (1940).
55. Colin G. Fink and Johnstone S. Mackay, "Photoelectric Cells Sensitive to Long Wave Length Radiation. The Bismuth Sulfide Cell," **77,** 299 (1940).
56. Lee Sutherlin and R. H. Cherry, "An Electrometer Tube for Laboratory and Industrial Use," **78,** 11 (1940).
57. Harold Graeme Bain, "Metallized Glass Oxygen Electrodes," **78,** 173 (1940).
58. Stanley Anderson and R. W. Manuel, "An Electrolytic Chromium Plate Thickness Tester," **78,** 373 (1940).
59. Eugene Willihnganz, "A Bridge for Measuring Storage Battery Resistance," **79,** 253 (1941).
60. G. L. Clark and P. G. Roach, "An X-Ray Study of the Structure of Rectifying Selenium Films," **79,** 355 (1941).
61. J. N. Mrgudich, "X-Ray Studies of Storage Battery Pastes," **81,** 165 (1942).
62. J. M. Pearson, " 'Null' Methods Applied to Corrosion Measurements," **81,** 485 (1942).
63. George Jernstedt, "High Speed Analysis and Control of Plating Solutions," **82,** 135 (1942).
64. V. F. Hanson and F. G. La Violette, "Location of Ground Faults on Series Electrolytic Cell Systems," **82,** 341 (1942).
65. W. N. Greer and A. L. Chaplin, "Some Factors Affecting Automatic *p*H Control," **83,** 67 (1943).
66. D. M. Nielsen, "Automatic Control of Electroplating Processes," **83,** 75 (1943).
67. M. E. Fogle, "Temperature Measurement and Control with Solid Photoelectric Cells," **83,** 77 (1943).
68. G. E. Huenerfauth, "Flexibility of the Cuprous Oxide Rectifier for Automatic Control Equipment in Electroplating," **83,** 87 (1943).
69. John Gorrell, "The Electrochemist Adopts Automatic Recording Devices Used in Medical Research," **83,** 95 (1943).
70. L. H. Fletemeyer, "A Load-Regulating System for Synchronous Converters," **83,** 101 (1943).
71. G. H. Fetterley, "High Temperature Resistivity Measurements on Compressed Granular Refractory Materials," **83,** 191 (1943).
72. E. H. Alexander, "Electronic Methods of Automatic Control of Industrial Processes," **83,** 205 (1943).
73. Howard F. McMurdie, "Microscopic and Diffraction Studies on Dry Cells and Their Raw Materials," **86,** 313 (1944).
74. J. N. Mrgudich and R. C. Clock, "X-Ray and Electron Microscope Evaluation of Carbon Blacks," **86,** 351 (1944).
75. Otto H. Müller, "Oxidation-Reduction Potentials Measured with the Dropping Mercury Electrode," **87,** 441 (1945).
76. A. E. Hardy, "Photoconductivity of Zinc-Cadmium Sulfide as Measured with the Cathode-Ray Oscillograph," **87,** 335 (1945).

7. Floyd Buckley and John K. Taylor, "Some Factors Affecting the Precision in Polarographic Analysis," **87,** 463 (1945).
8. E. L. Kirk, "Electric Metering of Electrolytic Pot Lines," **90,** 111 (1946).
9. Martin Tosterud and Ralph B. Mason, "An Aluminum Coulometer," **90,** 221 (1946).
10. A. P. Wangsgard and Thomas Hazen, "The Q-Meter for Dielectric Measurements on Polyethylene and Other Plastics at Frequencies up to 50 Megacycles," **90,** 361 (1946).
11. G. Benson, J. Gluck, and C. Kaufmann, "Electrical Conductivity Measurements of Carbon Blacks," **90,** 441 (1946).
12. Austin E. Hardy, "A Combination Phosphorometer and Spectroradiometer for Luminescent Materials," **91,** 221 (1947).
13. J. M. Gonzalez Barredo and John Keenan Taylor, "Automatic Recording of Titrations," **92,** 437 (1947).
14. H. A. Robinson, "Automatic Potentiometric Titrations," **92,** 445 (1947).
15. M. J. Astle, "The Polarograph in Organic Chemistry," **92,** 473 (1947).
16. G. A. Perley, "Hydrogen Gas Electrode Measurement," **92,** 485 (1947).
17. G. A. Perley, "An Industrial Salt Bridge Junction," **92,** 497 (1947).
88. J. J. Lingane, "Some Analytical Applications of Controlled Potential Electrolysis," **92,** 505 (1947).
89. John R. Musgrave and H. R. Harner, "A New Method for Particle Size Determination in the Sub-Sieve Range," **92,** 579 (1947).
90. Howard T. Francis, "An Electrolytic Thickness Tester for Plated Metal Coatings," **93,** 79 (1948).
91. S. L. Parsons, Alfred E. Martin, and S. N. Roberto, "Recording Spectroradiometers for Luminescent Materials," **97,** 41 (1950).
92. H. F. Beeghly, "An X-Ray Method for Determining Tin Coating Thickness on Steel," **97,** 152 (1950).
93. L. G. Glasser, "The Ultraviolet Method of Continuous Gas Analysis," **97,** 201C (1950).
94. Sidney Barnartt, "Gold-Plated Electrode for Measurement of Conductance of Electrolytes," **97,** 235 (1950).
95. D. J. Pye, "The Control of Bleach Manufacture by Oxidation Potential," **97,** 245 (1950).
96. F. S. McCarthy and G. A. Rice, "Liquid Chlorine Level Measurement," **97,** 249 (1950).,
97. J. M. Hildyard, "Instrumentation in a Modern Chlorine Handling Plant," **97,** 367 (1950).
98. G. A. Perley and E. L. Eckfeldt, "Measurement of and Effect of Temperature on Electrical Resistance of Glass Electrodes," **98,** 37 (1951).
99. Dimitrios Staicopoulos, Ernest Yeager, and Frank Hovorka, "Electronic Instrumentation for Overvoltage Measurements," **98,** 68 (1951).

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Current Affairs

Society Officers Start New Terms

J. C. WARNER

Chosen in the recent election, by mail ballot, and scheduled to take office at The Electrochemical Society meeting in Philadelphia, are J. C. Warner, the new President of the Society; H. H. Uhlig, elected Vice-President; and E. G. Widell, re-elected Treasurer. They will formally assume their offices at the annual business meeting following the Society luncheon on Tuesday, May 6.

Dr. Warner, President of Carnegie Institute of Technology, Pittsburgh, Pennsylvania, will replace Dr. Ralph M. Hunter of The Dow Chemical Company, Midland, Michigan. Dr. Hunter, in the status of Past President, will continue as a member of the Board of Directors of the Society.

Dr. Uhlig, Head, Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, will start his term as Vice-President and will serve with the two previously elected Vice-Presidents, R. J. McKay and Marvin J. Udy.

H. H. UHLIG

E. G. WIDELL

Mr. E. G. Widell, Radio Corporation of America, Harrison, New Jersey, has served as the Society's Treasurer for the past three years, and was re-elected to that office.

Gordon Research Conferences in June

The Gordon Research Conferences, sponsored by the AAAS, will hold a Corrosion Conference from June 16 to August 29 at Colby Junior College, New London, New Hampshire. The facilities of the college have been made available for the Conferences. The Gordon Research Conferences on Chemistry and Physics of Metals will be held on the same dates at the New Hampton School, New Hampton, N. H.

The Conferences, established to stimulate research in universities, research foundations, and industrial laboratories, consist of an informal type meeting for the scheduled lectures, and free discussion groups. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for recreation, reading, resting, or participation in discussion groups as the individual desires.

Applications for attending the Conferences should be sent to the Director, on or before *May 15*. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Letters should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 15 to September 1, mail should be sent to Colby Junior College, New London, New Hampshire.

* * *

Members of The Electrochemical Society who will lecture at the Conferences include: Norman Hackerman, F. L. LaQue, H. H. Uhlig, F. W. Fink, I. E. Campbell, R. H. Brown, T. P. May, Carl A. Zapffe, F. N. Alquist, C. E. Imhoff, Morris Cohen, and V. V. Kendall.

Kaiser Aluminum New Sustaining Member

A new Sustaining Member who has recently been welcomed by the Society is the Kaiser Aluminum and Chemical Corporation, Division of Metallurgical Research, Spokane, Washington.

The Kaiser Aluminum and Chemical Corporation is one of the major integrated producers of aluminum in this country. Nine aluminum plants located in Washington, California, Ohio, Maryland, Louisiana, and Jamaica, B.W.I., produce raw materials, primary aluminum, and mill products. Five other plants in California produce chemicals and basic refractories for industry. About 8500 persons are employed.

The modern, well-equipped laboratories of the Division of Metallurgical Research are located near Spokane, Washington. Fundamental and applied research is being undertaken in electrochemistry, metal finishing, corrosion, physical and process metallurgy, physical chemistry, and welding and joining.

Principal officers of the corporation are Henry J. Kaiser, president, D. A. Rhoades, vice-president and general manager, and T. J. Ready, Jr., vice-president and assistant general manager. Paul P. Zeigler is Director of the Division of Metallurgical Research, and Dana W. Smith and L. W. Eastwood are, respectively, Associate Director and Assistant Director of the Research Division.

Atom-Powered Submarine Plant for Westinghouse

Westinghouse Electric Corporation will build the complete power plant for the world's first atomic-powered submarine—the *U. S. S. Nautilus*—including both the nuclear reactor and the associated propulsion equipment, it was recently disclosed.

Previously, the company's Atomic Power Division had announced development, in cooperation with Argonne National Laboratory, of an experimental land-based nuclear reactor which will serve as the prototype of the actual submarine power plant. This experimental model is now under construction at the Atomic Energy Commission's reactor testing station near Arco, Idaho. The submarine reactor will be the product of the teamwork of many groups and the pooled efforts of many highly trained specialists, it was stated.

The company also reported that it will build the most powerful machinery ever designed for ship propulsion: the turbine and gear assembly for the nation's newest aircraft carrier, "*U. S. S. Forrestal.*" Other outstanding military developments reported include smaller, faster wakeless electric torpedoes; radar and fire-control devices for all-weather jet fighters; new and more powerful jet engines; and equipment for radio-controlled airborne lifeboats.

AIME Joint Conference in Pacific Northwest

The 1952 Pacific Northwest Conference of the AIME will be a joint meeting of the Industrials Minerals Division and, for the first time, the Metals Branch. The Conference will take place on May 8, 9, and 10, at the Davenport Hotel, Spokane, Wash.

An extensive program has been planned with technical sessions on May 9 and 10. May 8 is devoted mainly to plant trips. A cordial invitation has been extended to members of The Electrochemical Society to attend the Conference.

Hampel and Modjeska Announce New Firm

Clifford A. Hampel and R. Scott Modjeska have formed the Hampel-Modjeska Laboratories, in Chicago, for the purpose of conducting research and development studies, technological and economic evaluations, and consulting work for industry and government in the fields of industrial chemicals, electrochemical processes and products, and the recovery and utilization of strategic metals.

Hampel and Modjeska plan to undertake sponsored research programs in the fields of inorganic and organic heavy chemicals; the extraction metallurgy of titanium and other rare metals; the application of amalgam techniques to metallurgy and chemical production; electrodeposition; corrosion; metal finishing, etc.

Both men are well known in The Electrochemical Society, having held various offices in recent years. Clifford Hampel was Chairman of the Chicago Section of The Electrochemical Society in 1949–50, General Chairman of the Society's 96th National Meeting in Chicago in 1949, and has served on the Society's publicity, membership, and nominating committees. Mr. Modjeska is currently Chairman of the Chicago Section of the Society, in which he has been active for some time. O. W. S.

SECTION NEWS

Chicago Section

"What the Pioneers Missed" w the subject of an interesting discou on electrochemical problems, deliver by Dr. Ralph M. Hunter, Soci President, to the Chicago Section their March 7th meeting.

Dr. Hunter traced the progress of t electrochemical pioneers, praising t great job of process development some of the most widely used meta and chemicals. Year by year, he sai the production of such essential ite as chlorine, alkali, magnesium, a aluminum has increased unfalteringl each seven years in their history h seen an approximate doubling of t output of electrochemical industries.

But, he also pointed out, the ear electrochemists passed by some ver important areas in their desire to rea more concrete goals. To this day, ma of the "hows" and "whys" of electr chemical processes remain "Unexplor Territory."

Dr. Hunter discussed some of t unanswered questions which still pe sist in the industry. Through his wi experience in the basic processes, h was able to present a perspective on t subject that was both interesting an informative to his audience.

HOWARD T. FRANCIS, *Secretar*

● The announcement of this meeti was headed by a cleverly drawn cartoo showing the covered wagon of pione days, with signposts indicating t speaker's course.—ED.

Detroit Section

At a joint meeting on March 21, t Detroit Sections of The Electrochemic Society and the National Associati of Corrosion Engineers met at the E gineering Society for dinner and a tec nical meeting.

O. B. Ellis, Research Engineer, Arm Research Laboratories, addressed t group on the topic "Observations o Atmospheric Corrosion of Metals." M Ellis has been active on various AST committees and is well qualified t speak on this subject.

He discussed the effect of alloyi elements on atmospheric corrosion o low alloy steels, the effect of marin and industrial atmospheres on the co rosion of iron and zinc, and, finally, t effect of weather on corrosion of zinc

A. M. LINN, *Secretary-Treasur*

Midland Section

"Military Batteries" was the subject of a highly interesting address by Grenville B. Ellis, Chief, Power Sources Branch, Signal Corps Engineering Laboratories, Ft. Monmouth, N. J., before the Midland Section of the Society, on February 20.

Mr. Ellis opened his talk on "Military Batteries" by giving the history and development of the Leclanché primary cell. He discussed the early difficulties encountered in this cell and compared the present-day Leclanché cell with other Leclanché type primary cells, such as the alkaline zinc cell and the new magnesium primary cell, as well as with the Reuben-Mallory cell, which is not of the Leclanché type. For each of these cells, he emphasized the advantages in their applications, as well

GRENVILLE B. ELLIS

as their disadvantages. Further, he predicted future performance for each on the basis of present-day developmental research.

In addition to his discussion of the Leclanché and Leclanché type primary cells, Mr. Ellis explained and demonstrated the tremendous advancement made in the field of reserve type batteries. These were miniature high voltage cells which were capable of operating at very high drains for moderately short periods of time. The volume and weight limitations specified for these cells made this development a truly great advancement in the primary battery field.

Mr. Ellis also discussed many other types of primary and secondary cells that have been developed within the last decade. Among these were the thermal and nuclear energy primary cells, the zinc-silver peroxide caustic cell, and the nickel cadmium secondary cell which was developed by the Germans, but substantially improved by the Signal Corps.

Throughout his talk, the speaker profusely illustrated his speech by demonstrations with the various type cells and punctuated his remarks with interesting anecdotes.

In answer to a question, Mr. Ellis explained that the Signal Corps' present research program in primary and secondary batteries is not only paying its own way, but is also making money for the government through the increased savings in military expenditures on batteries.

W. R. PERRY, *Secretary-Treasurer*

New York Metropolitan Section

The biggest turnout the New York Metropolitan Section has ever had saw an educational motion picture in color entitled "Corrosion in Action," at the March 26th meeting. The picture explained the principles of corrosion in simple terms, with laboratory experiments, animation, and narration. It was arranged in three parts: (1) Electrochemical nature of corrosion, (2) galvanic corrosion, and (3) passivity. It was produced by the International Nickel Company.

A short introduction was given by Mr. F. L. LaQue, one of the foremost authorities in the corrosion field, who was largely responsible for the production of the film. This was the first public showing of the picture in this area and it was received with unstinted praise and enthusiasm by the audience.

A dinner and social hour preceded the showing of the film.

F. A. LOWENHEIM, *Secretary-Treasurer*

Niagara Falls Section

The members of the Niagara Falls Section enjoyed a dinner meeting at the Red Coach Inn on March 12, followed by a technical address by guest speaker Robert C. Wade of National Distillers Products Corp., Cincinnati.

Mr. Wade spoke on "Reactions of Sodium Dispersed over High Surface Solids." He is at present engaged in sodium use research and has done considerable work with chlorine products and with developments in organic and inorganic sodium fields.

A summary of his findings is given below:

The rate and completeness of reactions of sodium metal in heterogeneous systems are greatly affected by the surface area of sodium presented for reaction.

Surface area of sodium may be increased greatly by dispersing molten sodium in inert hydrocarbon media. The size of sodium particles obtained by this technique reaches a practical limit in the range of 1 to 10 microns. On the other hand, films of sodium having at least one dimension in "colloidal range" can be produced by absorbing sodium metal on solids of high surface area. Such sodium-solids dis-

ROBERT C. WADE

persions can be handled easily in fluidized solids systems at temperatures both above and below melting point of sodium.

Work described in this presentation indicates that sodium-solids dispersions are useful for preparing sodium hydride in the same vessel in which it is to be used in subsequent reactions; in the preparation of finely divided metals by reduction of metal halides; in the preparation of certain organometallic compounds; in the refining of hydrocarbons and ethers; and in certain catalytic processes.

* * *

Mr. Wade was accompanied to Niagara Falls by Dr. Virgil Hansley, also of National Distillers Products Corp. Both men are former members of this Section and were cordially greeted by their many acquaintances.

H. R. OSWALD, *Secretary-Treasurer*

Philadelphia Section

The Philadelphia Section held its third meeting of the current season on March 12, at the John Harrison Laboratory of Chemistry, University of Pennsylvania, with approximately 50 members and guests in attendance. As is customary, members and guests had an opportunity to meet the speaker of the evening at an enjoyable dinner gathering before the meeting.

Dr. John G. Gall, the Section Chairman, called on Dr. Hiram S. Lukens, Convention Chairman, who gave a progress report on the national convention

scheduled to be held in Philadelphia on May 4 to 8. He reported that plans are moving ahead very satisfactorily pointing toward an outstanding event from both a scientific and a social aspect.

The speaker of the evening, Dr. Park H. Miller, Jr., was next introduced by Chairman Gall. Dr. Miller is a member of the staff of the Physics Department of the University of Pennsylvania. His topic was "Semiconductors and Semiconducting Devices."

Dr. Miller opened with a review of the elementary concepts of the relationships between energy and interatomic distances, the Pauli exclusion principle, and the problem of the arrangement of electrons in atoms. He next discussed the large quantities of energy required to take an electron from the ground state (filled band) to an excited state (conduction band); one way of obtaining these energies is to shine light on the material. The effect of heat causing stronger absorption at the longer wavelengths was mentioned.

After defining a metal and an insulator Dr. Miller showed that semiconductors lie intermediate between these two extremes. He pointed out that basically semiconductors are of two classifications, intrinsic and impurity or extrinsic types. The former have excited and ground states close enough for thermal energy to impart the semiconduction properties. The latter must have small amounts of impurity present in order to act as semiconductors; there are donator and acceptor types depending on the location of the Fermi level with respect to the filled and conduction bands.

Many characteristics of these semiconductors were illustrated both with slides and with an ingenious model demonstrator constructed by Dr. Miller. Among the properties thus described were: electrical conduction, optical transmission, photoelectric response, luminescent emission, and the Hall effect.

Dr. Miller concluded his talk by mentioning the commercial aspects of semiconductors, along with their most obvious advantages and disadvantages. Applications such as their use as bolometers and photoconductors and in rectifiers and transistors were stressed. An interesting question and answer session of some duration followed the conclusion of the formal address.

(The abstract of Dr. Miller's talk appearing above was prepared by Mr. F. Curtis Snowden.)

E. L. Eckfeldt, *Secretary*

India Section

The India Section has announced that the first number (Volume 1, Number 1, January, 1952) of the *Bulletin of the India Section of The Electrochemical Society* has been issued.

* * *

The Mettur Chemical & Industrial Corporation, Ltd., Mettur Dam, has been welcomed as a patron of the India Section.

T. L. Rama Char, *Secretary-Treasurer*

PERSONALS

Irving G. Young has joined the Research Division of the International Resistance Company, Philadelphia, Pa. Mr. Young had been with the U. S. Electric Manufacturing Corp., New York, N. Y.

B. Sturm, formerly associated with the Burgess Battery Co., Freeport, Ill., is now a research chemist in the Materials Chemical Division of Oak Ridge National Laboratories, Oak Ridge, Tenn.

Arthur J. Kerbeck, Jr., who recently received a Ph.D. degree in chemical engineering from Columbia University, has accepted a position as research chemical engineer at E. I. du Pont de Nemours & Co., Wilmington, Del.

Felix Y. K. Chiang has accepted a position as electronic scientist, Wright Air Development Center, Wright-Patterson Air Force Base, Dayton, Ohio.

H. L. Turner is now attached to the Senior Research Staff at the Central Laboratory of the Ever Ready Company (G.B.) Limited in London. He was transferred from his position in charge of Process Control at the company's Battery and Flashlamp Factories in Wolverhampton.

James Fentress, formerly research assistant at Northwestern University, has joined Foote Mineral Company, Philadelphia, as sales engineer.

M. S. Thacker has been elected Chairman of the Mysore Centre of the Institution of Engineers (India).

Fred G. Brune has accepted a position as metal finishing engineer, Chrysler Jet Engine Plant, Dodge Division of Chrysler Corp., Detroit. He had formerly been superintendent of buffing, paint, and plating at the Marion Industries Division of Motor Products Corp., Marion, Ohio.

William B. Roberts has left Sylvania Electric Products Inc., Flushing, N. Y., to join P. R. Mallory & Co. Inc., Rectifier Division, Indianapolis, Ind.

John J. Chapman, Institute of Cooperative Research, The Johns Hopkins University, Baltimore, Md., has been appointed Divisional Editor on the Journal for the Electric Insulation Division, succeeding former Editor R. R. Ralston.

NEW MEMBERS

In March 1952, the following were elected to membership in The Electrochemical Society:

Active Members

Edward G. F. Arnott, Westinghouse Lamp Division, mailing add: 40 Oakwood Ave., Upper Montclair, N. J. (Electronics and Theoretical Electrochemistry)

Edward G. Bohlman, Oak Ridge National Laboratory, P.O. Box P, Oak Ridge, Tenn. (Corrosion)

Arthur A. Burr, Rennsselaer Polytechnic Institute, Troy, N. Y. (Electrodeposition)

T. G. Catlaw, Allen B. Du Mont Laboratories, mailing add: 54 Euclid Ave., Hackensack, N. J. (Electronics)

Arnold I. Friedman, General Electric Co., mailing add: 2980 E. 132nd St., Cleveland 20, Ohio (Electronics). Formerly Associate Member

Albert W. Friend, Magnetic Metals Co., Hayes Ave. at 21st St., Camden 1, N. J. (Electric Insulation, Electrodeposition, Electronics, Electro-Organic, Electrothermic, Industrial Electrolytic, and Theoretical Electrochemistry)

Andrew P. Honchar, National Lead Co., mailing add: 371 Shoreland Circle, Laurence Harbor, N. J. (Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

Thomas E. Keane, Gould-National Batteries, Inc. 467 Calhoun St., Trenton 7, N. J. (Battery)

Marjorie S. Malmberg, National Bureau of Standards, 403 East Bldg.

Washington, D. C. (Battery and Theoretical Electrochemistry)

Wayland C. Marlow, Owens-Corning Fiberglas Corp., Newark, Ohio (Battery, Electric Insulation, and Electronics)

Joseph B. McAndrews, Armour Research Foundation, 35 W. 33rd St., Chicago 15, Ill. (Corrosion)

Richard V. Montieth, General Motors Corp., mailing add: 2310 W. 65th, Indianapolis, Ind. (Electrodeposition)

John J. Newport, Electrochemical Engineering Department, Dow Chemical Co., Freeport, Texas. (Electro-Organic, Industrial Electrolytic, and Theoretical Electrochemistry)

Charles P. Patterson, Columbia Steel Co., mailing add: 3101 Withers Ave., Lafayette, Calif. (Electronics)

N. B. Shivaraman, Tata Chemical Ltd., Mithapur (Samastra), India (Corrosion, Electrodeposition, and Industrial Electrolytic)

James Woodburn, Jr., Great Lakes Carbon Corp., Niagara Falls, N. Y. (Industrial Electrolytic)

Reinstatements

Georges Chaudron, Laboratorie de Chimie Appliquée, 11 Rue Pierre-Curie, Paris 5, France

John G. Dean, Dean Research Services, 8 Beaumont Circle, Tuckahoe, N. Y. (Electrodeposition)

Robert T. Gore, Metal and Thermit Corp., Box 471, Rahway, N. J. (Electrodeposition)

Associate Members

Charles K. Bon, Dow Chemical Co., mailing add: 468 Swede Rd., Midland, Mich. (Industrial Electrolytic)

George A. Green, Great Lakes Carbon Corp., Niagara Falls, N. Y. (Industrial Electrolytic)

Arthur J. Kerbecek, Jr., E. I. du Pont de Memours & Co., mailing add: 213 Thomas Drive, Apt. B., Monroe Park, Wilmington 6, Del. (Electrodeposition). Formerly Student Associate Member

Charles W. McCutchen, Electrochemical Engineering Department, Dow Chemical Co., Freeport, Texas (Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

Student Associate Member

James C. Lamb III, Massachusetts Institute of Technology, mailing add: 284 Westgate W., Cambridge, Mass. (Corrosion)

BOOK REVIEWS

ELEMENTS OF PHYSICAL METALLURGY by Albert G. Guy. Published by Addison-Wesley Press Inc., Cambridge, Mass., 1951. 293 pages, $6.50.

This book is proposed by the author as an introduction to physical metallurgy, not only for those whose main interest is metallurgy, but for general engineering students. As such it covers a very broad field. It is obvious that it cannot go into any great detail on any particular phase of the subject, but this is no reflection on the author because such detail belongs in the more advanced and specialized courses. The choice of material to be included shows a great deal of care, judgment, and the effects of experience in teaching.

Practically all of the fundamentals of physical metallurgy are touched upon in one way or another. The writing is lucid and very readable. An excellent appendix dealing with the literature of metallurgy will be exceedingly helpful.

The book is divided into 14 chapters and the page size is sufficiently large to make 2-column pages. It may be a small matter but it is, after all, exceedingly convenient to have a book that will open out flat. The general format is pleasing.

Some small criticism may be made. The first is that the tables and the size of type therein are too small. Second, the "photographic" reproductions often lack contrast and in many cases are too small; also the same lack of clarity and size are a distinct drawback in the case of many of the photomicrographs. It might be worth while in the long run to include answers to the numerical problems.

To cover the material within the pages of this book thoroughly in a standard one-year college course will be no task for a sluggard. However, it is believed that any student who makes a serious effort to encompass the material will be amply rewarded.

EARLE E. SCHUMACHER

ULTRASONICS by P. Vigoureux. Published by John Wiley & Sons, Inc., New York, 1951. vi plus 163 pages, $4.00.

This book on ultrasonics is an introduction to the apparatus, techniques, some of the experimental results for gases and liquids, and a rather complete description of the theories of relaxation effects in gases and liquids. The principal topics covered are piezoelectric transducers—principally quartz—some original work on the equivalent circuit of magnetostrictive transducers; the classical propagation equations and the losses associated with viscosity and heat conduction; the relaxations associated with intermolecular processes such as the transfer of energy from longitudinal to rotational and internal vibrations; the methods for measuring the velocity and attenuation in gases and liquids; and measurements for gases and liquids and their interpretation. The last chapter, discussing the measurements and the most recent interpretations for the relaxation effects in liquids, is the most valuable chapter. The book does not discuss measurements in solids or the effects of large amplitude vibrations.

As an introduction to the techniques and results for gases and liquids, the book is a very readable and complete account.

W. P. MASON

LITERATURE FROM INDUSTRY

METAL CLEANING. A newly revised brochure entitled "Cleaners for Effective Metal Cleaning" is available for those concerned with cleaning metal prior to electroplating, anodizing, painting or otherwise applying decorative or protective coatings. Included are six different methods of metal cleaning; a table listing the cleaners to use for various metals; electrocleaners, etc. Hanson-Van Winkle-Munning Co. P-29

'UNITIZED' LOW-VOLTAGE SWITCHGEAR. Illustrated 30-page booklet, "'Unitized' Low-Voltage Metal-Enclosed Switchgear" explains just what the equipment is and outlines its applications; describes the types DB and DA drawout De-Ion air circuit breakers that are the heart of "unitized" switchgear. Current ratings, etc., given. Westinghouse Electric Corp. P-30

HAND PYROMETER. Bulletin GEC-836 describes a new hand pyrometer with two scale ranges for rapid and convenient measurement of surface, liquid, gas, and molten-metal temperatures. Scale ranges are 0–500 F and 0–1500 F. General Electric Company. P-31

NONISOLS. Technical bulletin describes nonionic surface active agents of the polyoxyalkylene fatty ester type: emulsifiers and interfacial tension depressants, spreading agents, detergents, thickeners, etc. Alrose Chemical Co. P-32

GALVANOMETERS AND DYNAMOMETERS. Complete line of standard galvanometers, dynamometers, d-c indicating amplifiers, and accessories for use in null-balance or calibrated deflection measurements is presented in revised, 20-page Catalog Section ED. Leeds & Northrup Co. P-33

ALUMINUM COATING. Folder on "Alodine," describes this protective coating for aluminum, and its applications. This chemical has recently been made a stock item by the Navy. American Chemical Paint Co. P-34

LEAD CLAD METALS. New 22-page booklet, "The History and Development of Ferrolum Lead Clad Steel and Cupralum Lead Clad Copper" offers essential information to engineers, designers, and technicians for solving many design and process problems in which lead clad metals are used. Knapp Mills, Inc. P-35

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

TITANIUM RESEARCH

Physical or inorganic chemist for research and development on electrolytic processes for producing titanium. Experience or graduate training in electrochemistry is desirable.

National Research Corporation

70 Memorial Drive **Cambridge 42, Mass.**

TREASURER'S REPORT* FOR 1951

The Auditor's Report appeared in the April 1952 JOURNAL.

Canadian Convention Fund

Bank Balance, 1/1/52		$1,104.20

THE CANADIAN BANK OF COMMERCE
25 King Street West, Toronto,
Ontario, Canada

Corrosion Handbook Fund

Total Corrosion Handbook Fund, 1/1/51		$12,612.36
Corn Exchange Bank		
USA Bonds Series F (earmarked in safe deposit box)		10,471.37
New York Savings Bank		
Balance, 1/1/51	$ 987.19	
Credit:		
Interest for 1951	46.47	
Royalties for 1951	2,928.60	
	3,962.26	
Debit: Prizes, etc.	2,033.80	
Balance, 1/1/52		1,928.46
Total Corrosion Handbook Fund, 1/1/52		$12,399.83

Columbus Convention Fund

USA Gov. Bonds Series F (earmarked in safe deposit box)		$ 400.00

CORN EXCHANGE BANK
102nd Street at Broadway, New York, N. Y.

Edward Weston Fellowship Fund—for 1951

Total Weston Funds available for Fellowship 1/1/51		$ 2,296.91
*Capital Funds Securities, 1/1/52**		
$11,881.88	In Central Hanover Bank & Trust Co. Trust Fund A—1160 units	
1,836.66	AC 1330 Brook Ave., Bronx, N. Y. NYT & M Co.	
1	Prudence 422–34 E. 86th St., New York, N. Y., allowed claims	

* The Hanover Bank, Trustees, 70 Broadway, New York 15, N. Y.

The Hanover Bank, Trustees		
Principal Account Balance, 1/1/51	$ 182.94	
Credit: Sold		
2800 USA Treasury Bonds 2½% 4/19/51	2,756.25	
9000 USA Savings Bonds Series G	9,000.00	
	11,939.19	
Debit: Bought 1160 units CHBT Co. Trust Fund A 5/2/51	11,881.88	
Principal Account Balance, 1/1/52	57.31	
Checking Account Balance, 1/1/51	1,128.56	
Credit: Deposit from Income Account, 9/11/51	331.80	
Checking Account Balance, 1/1/52		$ 1,460.36
Income Account Balance, 1/1/51	146.53	
Credit:		
Interest USA Bonds	135.92	
Dividends H. B. & Trust Co., Fund A, 5/5/51 to 10/1/51	160.17	
	442.62	
Debit:		
Hanover Bank Commission at 5% on Income	17.46	
Deposit to Checking Account, 9/11/51	331.80	
	349.26	
Income Account Balance, 1/1/52		93.36
The Hanover Bank Balance for Fellowship, 1/1/52		1,553.72
Seamen's Bank for Savings		
Income Balance, 1/1/51	1,021.82	
Credit: Interest for 1951	20.53	
Income Balance, 1/1/52		1,042.35
Total Weston Fund Available for Fellowship, 1/1/52		$2,596.07

Edward Goodrich Acheson Fund—for 1951

*Capital Funds Securities—1/1/52**

$ 5,000.	USA Savings Bonds Series F, no interest; due 10/1/53. Registered.
10,000.	USA 2½% Savings Bonds Series G due 11/1/54. Registered.
2,000.	Pennsylvania Railroad Co. 3¼% General Mortgage Bond, Series F. Due 1/1/85.
2,000.	American Telephone & Telegraph Co. 2¾% Debenture due 10/1/75.
13 shs.	American Can Co. 7% Cum. Pfd.
14 shs.	Corn Products Refining Co. 7% Cum. Pfd.
10 shs.	Eastman Kodak Co. 6% Cum. Pfd.
10 shs.	Ingersoll Rand Co. 6% Cum. Pfd.
25 shs.	International Harvester Co. 7% Cum. Pfd.
20 shs.	National Lead Co. Class A 7% Cum. Pfd.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Participating Certificate, Series 2-7165 Bond & Mortgage. Only remaining asset is General Claim.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Series 3-6902 due 3/1/38. 5½%
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Certificate in Bond & Mortgage of Chatsworth Gardens Corp. Series 6-6972 Certificate #296. Only remaining asset is General Claim against the former guarantor.

* Guaranty Trust Company of New York, Custodian.
Fifth Ave. at 44th St., New York 18, New York

Acheson Fund Total Balance, 1/1/51		$ 3,158.66
Guaranty Trust Co., *Custodian*		
Income Balance, 1/1/51 (includes Prin. Fds. of $97.43)		2,453.49
Credit: Dividends plus interest		991.50
		3,444.99
Debits: Custodian Charges		72.00
Income Balance, 1/1/52 (includes Prin. Fds. of $97.43)		3,372.99

TREASURER'S REPORT FOR 1951 (*continued*)

East River Savings Bank

Principal Funds Balance, 1/1/51	$ 705.17
Interest for 1951	14.17
Principal Funds Balance, 1/1/52	719.34
Acheson Fund Total Balance, 1/1/52	$ 4,092.33

Roeber Research Fund

Bank Balance, 1/1/51	$ 5,106.76
Credit: Interest for 1951	102.63
Bank Balance 1/1/52	$ 5,209.39

East River Savings Bank
Amsterdam Ave. at 96th Street, New York N. Y.

Joseph W. Richards Memorial Fund

Bank Balance 1/1/51	$ 3,685.4
Credit: Interest for 1951	72.0
	3,757.4
Debit: J. O'M. Bockris 4/9/51	100.0
Bank Balance 1/1/52	$ 3,657.4

Central Savings Bank
Broadway at 73rd Street, New York, N. Y.

* * *

RECENT PATENTS

Selected for electrochemists by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

January 1, 1952

Conti, G., 2,580,518, Söderberg Electrode Suspension

Drummond, A. P., 2,580,664, Dry Cell

Konrad, E. H., and Kaye, W. H., 2,580,681, Method of Treating the Electrolyte in the Electrodeposition of Iron

Leonard, W. E., 2,580,801, Method of Making Lustrous Steel Music Wire

Battey, A. J., 2,581,229, High-Temperature Quick Action Thermocouple

January 8, 1952

Lohr, J. M., 2,581,420, Alloys

Larsen, G. T., 2,581,490, Electrolytic Process of Stripping Metallic Coatings from a Ferrous Metal Base

Nissim, R., 2,581,597, Process for the Reduction of Iron Ores and the Like by Carbon

Gorin, E., 2,581,650, Method of Converting Carbon to Electrical Energy

Gorin, E., 2,581,651, Integrated Gasification Electro-Chemical System

Kahn, M., 2,581,863, Process for Electrodepositing Uranium Dioxide

Glegg, G. L., 2,581,950, Method and Apparatus for Determining Water Content of Concrete in Fluid State

Emery, S. B., 2,582,020, Electrolytic Polishing

Schwinn, F. W., 2,582,072, Battery Case

Hansgirg, F. J.; Hansgirg, J. M., administratrix of said Hangsgirg, F. J., deceased, 2,582,120, Production of Magnesium

January 15, 1952

Chester, A. E., and Reisinger, F. F., 2,582,233, Electroplating Copper

Robertson, J. W., 2,582,281, Electric Field Heat-Treatment of Liquids

Frary, F. C., 2,582,376, Process of Producing Gallium

Brown, R. W., 2,582,377, Recovery of Gallium from Alkali Metal Aluminate Solutions

Brown, R. W., 2,582,378, Process of Producing Gallium

Udy, M. J., 2,582,469, Metallurgy

Torchet, P., 2,582,661, Method for Electrolytically Refining Aluminum

Bailey, B. L., 2,582,764, Manufacture of Carbon Electrodes

Murphy, H. P., 2,582,845, Means for Reducing Local Action in Lead Acid Storage Batteries

Rose, A., 2,582,850, Photocell

Van der Pyl, E., 2,582,855, Electric Tunnel Kiln

Guanella, G., and Lardelli, O. A., 2,582,903, Device for Producing Chemical Reactions in a Flowing Gas by Electrical Means

January 22, 1952

Rieger, E. W., Re. 23,456, Apparatus for Electrocoating Striplike Material

Ellis, G. B., 2,582,973, Sealing Means for Primary Alkaline Dry Cells

Lytle, W. O., 2,583,000, Transparent Conducting Films

Olsen, K. M., 2,583,008, Asymmetric Electrical Conducting Device

Olsen, K. M., 2,583,009, Asymmetric Electrical Conducting Device

Townsend, M. A., 2,583,029, Method of Preparing Glow Discharge Devices

Richardson, R. P., 2,583,063, Voltaic Battery

Heise, G. W., Schumacher, E. A., and Wilson, H. R., 2,583,098, Treatment of Waste Pickle Liquor

Oliver, J. P., 2,583,099, Pre-electrolysis Treatment of Pickle Liquor

Wilson, H. R., 2,583,100, Treatment of a Metallic Cathode to Receive Electrodeposited Metal

Oliver, J. P., 2,583,101, Electrolyt Cell

Patnode, H. W., 2,583,276, Method Determining Formation Factor of I regular Rock Samples

Wyllie, M. R. J., and Hogg, G. A 2,583,284, Method for Determini a Parameter of Earth Formatio Penetrated by a Borehole

Cooper, H. S., 2,583,473, Aluminu Magnesium Alloys

Yoder, J., 2,583,525, Method for Sh ing and Terminating Tubular D vices.

January 29, 1952

Lukens, H. S., 2,583,581, Metal Coati

O'Connor, F., 2,583,589, Electric Cu rent Generator

EMPLOYMENT SITUATIONS

Please address replies to box shown % The Electrochemical Society, Inc. 235 W. 102nd St., New York 25, N. Y.

Positions Available

Research Head for confidential project in organic electrochemistry. Requires Ph.D. or equivalent industrial experience to head original research requiring exceptional talent, independent thinker, strong theoretical background. $5000-$6000. Location: Detroit. *Reply to Box No. A-237.*

Senior Chemical Engineer. Masters degree or Ph.D. preferred, with 10 or more years of experience in technical operation of all types of chlorine cells. Some production experience desirable, as well as the ability to direct other technical men. Excellent hospitalization, surgical and life insurance, and pension benefits. Michigan area. Please give full details in first letter. *Reply to Box A-238.*

Editorial

The Present Status of Electro-Organic Chemistry

In looking back over the past fifty years it is apparent that activity in the field of electro-organic chemistry reached a peak in the early part of the twentieth century and then suffered a decline. From that period on there has been a small but steady output of papers for the most part by a few investigators, until recently when interest has been renewed. At the beginning of the period most of the research was carried out in Germany, but is now in progress all over the world. Publication in our own Society was sporadic until about 1920, but has been steady ever since. About twelve years ago sufficient interest was shown to warrant the establishment of an Electro-Organic Division, which, while still small, is very active. For several years authors were invited by the Division to contribute to its symposia papers devoted almost exclusively to studies of reactions carried out on a preparative scale. Recently, however, it was decided to broaden the scope of the symposia to include studies on a micro scale, in particular, on organic polarography. The response has been most gratifying. The two parts of the field are in many instances mutually complementary with the result that more rapid progress should be made in elucidating the mechanisms of electro-organic reactions.

Although research has been carried out in the field of electro-organic chemistry for over one hundred and fifty years, its volume has been very small. The number of papers published is only a small fraction of those on electrodeposition, for example. The consequence has been that electro-organic chemistry today is in very much the same purely experimental state as organic chemistry in the middle of the nineteenth century when it was possible to prepare new compounds by the simplest operations, such as the nitration of toluene. Even such elementary factors as the influence of the cathode material and accompanying conditions on the course of the reduction of many types of organic compounds have never been studied. Many other illustrations of lack of development could be given. A natural result of the present state of knowledge in the field is the small number of industrial applications. It is to be hoped that by the end of the next half century the fundamentals of electro-organic chemistry will have been explored to the extent that a general theory may be proposed.

—Sherlock Swann, Jr.

Sustaining Members of The Electrochemical Society

Air Reduction Company, Inc., New York, N. Y.

Ajax Electro Metallurgical Corporation, Philadelphia, Pa.

Alloy Steel Products Company, Inc., Linden, N. J.

Aluminum Company of America, New Kensington, Pa.

American Platinum Works, Newark, N. J.

American Potash & Chemical Corp., Los Angeles, Calif.

American Zinc, Lead and Smelting Company, St. Louis, Mo.

Atlas Powder Company, Wilmington, Del.

Bell Telephone Laboratories, New York, N. Y.

Bethlehem Steel Company, Bethlehem, Pa.

Buffalo Electro-Chemical Company, Buffalo, N. Y.

Burgess Battery Company, Freeport, Ill.

Canadian Industries Limited, Montreal, Canada

Chrysler Corporation, Detroit, Mich.

Columbia-Southern Chemical Corporation, Pittsburgh, Pa.

Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

Crane Company, Chicago, Ill.

Diamond Alkali Company, Pittsburgh, Pa.

Dow Chemical Company, Midland, Mich.

E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

Electric Auto-Lite Company, Toledo, Ohio

Electric Storage Battery Company, Philadelphia, Pa.

The Eppley Laboratory, Newport, R. I.

General Chemical Division, Allied Chemical & Dye Corporation, New York, N. Y.

General Electric Company, Schenectady, N. Y.

Gould-National Batteries Inc. Depew, N. Y.

Graham, Crowley & Associates, Inc., Chicago, Ill.

Great Lakes Carbon Corporation, Niagara Falls, N. Y.

Hanson-Van Winkle-Munning Company, Matawan, N. J.

Harshaw Chemical Company, Cleveland, Ohio

Hooker Electrochemical Company, Niagara Falls, N. Y.

Houdaille-Hershey Corporation, Detroit, Mich.

International Nickel Company, New York, N. Y.

International Graphite & Electrode Corporation, St. Marys, Pa.

International Minerals & Chemical Corporation, Chicago, Ill.

Kaiser Aluminum & Chemical Corp., Division of Metallurgical Research, Spokane, Wash.

Mathieson Chemical Corporation, Niagara Falls, N. Y.

McGean Chemical Company, Cleveland, Ohio

Metal & Thermit Corporation, New York, N. Y.

Monsanto Chemical Company, St. Louis, Mo.

National Carbon Division, Union Carbide and Carbon Corporation, New York, N. Y.

National Cash Register Company, Dayton, Ohio

Niagara Alkali Company, Niagara Falls, N. Y.

Norton Company, Worcester, Mass.

Pennsylvania Salt Manufacturing Company, Philadelphia, Pa.

Potash Company of America, Carlsbad, N. Mex.

Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y.

Stackpole Carbon Company, St. Marys, Pa.

Standard Steel Spring Company, Coraopolis, Pa.

Stauffer Chemical Company, San Francisco, Calif.

Sylvania Electric Products, Inc., Bayside, N. Y.

Tennessee Products & Chemical Corporation, Nashville, Tenn

Udylite Corporation, Detroit, Mich.

Union Carbide Company, Electrometallurgical Division, New York, N. Y.

United Chromium, Inc., New York, N. Y.

Vanadium Corporation of America, New York, N. Y.

Victor Chemical Works, Mt. Pleasant, Tenn.

Western Electric Company, Inc., Chicago, Ill.

Western Electrochemical Company, Los Angeles, Calif.

Westinghouse Electric Corporation, E. Pittsburgh, Pa.

Westvaco Chemical Division, Food Machinery and Chemical Corporation, New York, N. Y.

Willard Storage Battery Company, Cleveland, Ohio

Wyandotte Chemicals Corporation, Wyandotte, Mich.

Fiftieth Anniversary

ELECTRO-ORGANIC CHEMISTRY

*H. Jermain Creighton**

Introduction

During the first half of its existence The Electrochemical iety played but little part in the development of electro-anic chemistry. Throughout its first decade only a single tro-organic paper appeared in the Society's TRANSAC-ns (1). During its second decade an awakening concern this phase of electrochemistry is indicated by a small in-se in the published papers, as well as by a symposium on electrochemical production of organic compounds held, 915, by the New York Section of the Society, jointly with local sections of the American Chemical Society and the iety of Chemical Industry (2). But it was not until the 0's, however, that a marked interest in electro-organic mistry was manifest. The steady growth of this interest ich then followed, coupled with an increase in the number papers in this field which were presented at meetings of Society, led to the formation of, first, a Technical Com-ttee and then a Division of Electro-Organic Chemistry. Since its inauguration, in 1940, the Division of Electro-anic Chemistry has had the following chairmen:

1940–41	Alexander Lowy
1941–42	A. F. G. Cadenhead
1943–44	H. Jermain Creighton
1944–46	Sherlock Swann, Jr.
1946–48	N. M. Winslow
1948–50	C. A. Crowley
1950–	Hans R. Neumark

During the past fifty years, more especially for the period The Electrochemical Society's active interest in electro-anic chemistry, this phase of electrochemistry has pro-ssed steadily. This has been due largely to extensive and tematic investigations of the influence of a number of olarization variables on the nature and efficiency of tro-organic reactions. Some of the results of these and er studies, to which members of the Society have made ditable contributions, are presented in the short review ich follows.

Electrode Potential

The first systemmatic study of electro-organic synthesis is be found in the classic investigation by Haber of the trolytic reduction of nitrobenzene (3). In this he showed at the nature of the reduction of this depolarizer depends y largely on the magnitude of the cathode potential; and at by regulating the electrode potential various "grades of lucing [or oxidizing] energy" may be secured. The electrode tential is of prime importance in bringing about desired tro-organic reactions. Since, moreover, the influences of st other variables are contained in the electrode potential), the use of a specially designed circuit has been suggested the automatic control of this variable (5).

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The nature of the electrode material is of marked significance in determining the course of the depolarization process. By employing as electrodes those materials with high overpotentials, powerful reducing or oxidizing energies may be secured. This is especially important when the depolarizer is a substance which is reducible or oxidizable only with difficulty. Many substances can be reduced, for example, only at cathodes of metals of high hydrogen overpotential: pyridine and compounds containing the keto group require a cathode of mercury or lead (6); the reduction of hexoses to their corresponding hexatols necessitates the use of mercury, amalgamated lead or a few other metals of high hydrogen overpotential (7); the use of metals of the highest overpotential is essential for securing the greatest yields of *n*-pentane from methyl *n*-propyl ketone (8). It is of interest that in a solvent of sulfuric-glacial acetic acid reduction of benzophenone takes place with high yields at cathodes of copper or nickel, whereas in an aqueous medium marked reduction occurs only at cathodes of high hydrogen overpotential (9). For the reduction of methyl propyl ketone, tin is an efficient cathode material in sulfuric-glacial acetic acid but, in spite of its high hydrogen overpotential, this metal is inactive in aqueous solution (10).

The efficiency of the reduction of sorbic acid at different cathode materials is approximately as follows:

Cu, Hg > Cd > Sn > Zn > Tl ≫ Pb, Ag, Fe, Al, Mg, Pt, Ni (smooth), no appreciable reduction taking place at cathodes of the last seven metals (11). Notwithstanding the resemblance between this series and that for hydrogen overpotential, there is a striking deviation in the relative positions of copper and lead. This singular behavior of copper is also met with in the reduction of nitrocompounds, where it is a most effective cathode material. Since at this cathode the current efficiency of the reduction of nitrobenzene increases with rise in temperature whereas the overpotential of the electrode decreases, it would seem that in this reduction overpotential must play a secondary role (12).

For difficult reductions it is essential to ensure the purity of the cathode materials used, since their efficiency is impaired greatly, if not entirely, by the presence of low overpotential impurities (13). Mere traces of impurities of this nature even when present in the electrolyte can, due to their electrodeposition, cover the cathode surface with a monolayer of low overpotential material. The reduction of caffeine, for example, is almost completely inhibited when traces of salts of copper, silver, or platinum are contained in the electrolyte (4). In the reduction of acetone at a lead-coated copper cathode, the presence of 8.4 mg/L of iron in the aqueous-sulfuric acid catholyte decreases the current efficiency of pinacol formation from 45.3 per cent to 33.8 per cent over a six-hour interval (14).

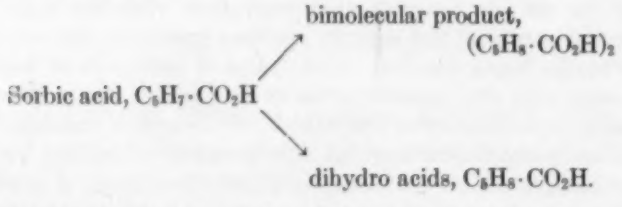
Physical Condition of the Electrode

During the past fifteen years a number of investigations have been carried out for the purpose of establishing whether the physical condition of the cathode material (produced by electrodeposition, casting, rolling, extrusion, machining, etching, annealing, carburizing, quenching, and other treatments) may exert an influence on the efficiency of depolarization (15). While as yet no general conclusions have been reached, it has been found that in some electro-organic reductions physical characteristics of the cathode material, such as crystal structure, crystal orientation, and internal strain, do affect electrode activity.

In the study of the reduction of methyl *n*-propyl ketone to pentane at cathodes of certain binary alloys, the crystal structure of which varies widely with composition, it has been found that: variations in the composition of the cathode from 100 per cent mercury to 100 per cent cadmium are accompanied by yields of pentane which, when plotted against the composition of the alloy, show inflections that correspond with the phase changes in the alloy (16); the relative constancy of pentane yields at a bismuth-cadmium cathode over the composition range, 10–90 per cent cadmium, is traceable to the two-phase structure of the alloy (17). In the electrolytic reduction of hexoses, for the maximum yield of hexahydric alcohols, a cathode having a macro etch is preferable to one having a surface of a colloidal deposit; an electrodeposited zinc cathode (110 face parallel to the surface) is 30 per cent less active than one of cast metal (001 face parallel to the surface); and the activity of a lead cathode increases with increase in grain size, but the reverse holds for the reduction of fructose at a cadmium cathode (18). Microphotographs of cadmium-bismuth cathodes indicate that the grain size of the very dilute cadmium-bismuth solid solution is not a factor in determining their efficiency in the reduction of methyl *n*-propyl ketone (17). In the reduction of nitrobenzene at cathodes of different metals, the current yield of aniline has been found first to increase slowly and then to diminish as the internal strain of the electrode increased (19).

At cathodes formed by the electrodeposition of a film of lead (0.12 g/dm^2) on copper, acetone is reduced in an aqueous-sulfuric acid electrolyte with high pinacol and low isopropyl alcohol efficiency. As electrolysis proceeds, the initial shiny surface of the cathode becomes black, spongy, and powdery, and the current efficiencies slowly change, reaching at the end of five hours a maximum of 65–68 per cent for pinacol formation and a minimum of 8–10 per cent for isopropyl alcohol formation. More extended electrolysis results in a reversal of these trends (14).

The electrolytic reduction of sorbic acid may yield both dihydro acids and a bimolecular product (probably formed by the dimerization of radicals):



In this reduction, in alkaline solution, appreciable amounts of bimolecular product are obtained only at a mercury cathode (20). That this unique behavior of mercury is in some manner associated with its liquid state is supported by the fact that, while bimolecular product is formed at a solid gallium cathode, a very marked increase in its yield takes place as the te perature of this cathode passes through its melting point (1

Velocity of Depolarization

The velocity of depolarization is an important factor electrochemical reactions. In the case of reduction proces it is evident that if the discharge of hydrogen ions at cathode takes place more rapidly than the reaction betw the active hydrogen thus formed and the depolarizer, concentration of the former must gradually rise and with the cathode potential. When this becomes sufficiently hi gaseous hydrogen will be liberated, thus diminishing current efficiency of reduction, since molecular hydrogen h little or no reducing power under conditions which usua prevail. If, however, the catholyte contains a depolari which reacts sufficiently rapidly with the active hydrog the cathode potential will not reach the value required the evolution of gaseous hydrogen. The advantages of hig operating temperatures, which increase the rate of reducti of the depolarizer, and of cathode materials with high hyd gen overpotentials, which raise the potential at which gase hydrogen is evolved, are obvious.

Since increasing the current density not only raises t cathode potential (perhaps to the value for hydrogen evol tion), but also decreases the concentration of the depolari in the vicinity of the cathode, electrolytic reduction is, general, more rapid and complete and depolarization e ficiency higher, the lower the current density (21). Evidentl a high depolarizer concentration and effective stirring a also advantageous.

Sometimes the desirable value to be selected for a giv depolarization variable is dependent on the values fixed f other variables. For instance, in the electrolytic reduction glucose in alkaline solution, although the rate of manni and sorbitol formation is not raised by increasing either t temperature or the current density singly, it may be marked improved by increasing these variables simultaneously. Ho ever, it does not suffice to select any two values of temper ture and current density at random. The particular valu to be employed depend, in a given case, upon both the initi concentration of the glucose in the catholyte and the rat of the cathode area to the catholyte volume (22).

Catalytic Influences

In addition to its overpotential, the catalytic power of t electrode material may play a decisive role in depolarizatio In fact, the end result frequently depends largely on th factor. At a cathode of nickel (low hydrogen overpotenti or mercury (high hydrogen overpotential) oleic acid is r duced but imperfectly, whereas at a cathode of palladium platinized platinum (very low hydrogen overpotential) r duction takes place smoothly with a good yield of stear acid (23). In the electrolytic reduction of nitrobenzene i alcoholic solution azoxybenzene, together with azobenze is formed at cathodes of platinum, nickel, or mercury; und the same conditions, hydrazobenzene is formed at zinc, ti or mercury; at a copper cathode the principal reducti product is aniline (24). At anodes of nickel or copper oxid tion of alcohol, α-glycol and α-hydroxyacids first takes pla without splitting of the carbon chain, while at bright platinu the molecule is severed (25). By the addition of 12 per ce of iron to a nickel cathode, the efficiency of the reduction nitrobenzene in alcoholic solution is raised from 58 per ce to 72 per cent (26).

Electro-organic reactions may sometimes be accelerate

by the use of hydrogen or oxygen "carriers"—salts containing an ion of variable oxidation number which react readily with the organic substance and then are regenerated at one of the electrodes. By this means the efficiency of the oxidation of terpene hydrocarbons at a lead dioxide anode is increased by the addition of a small quantity of a ceric salt to the electrolyte, due presumably to the reduction of the ceric ion by the hydrocarbon and its subsequent preferential oxidation at the anode, this cycle then being continued (27). Among the carriers most frequently employed in electro-organic reactions are salts of chromium, titanium, tin, cerium, vanadium, and iron (28).

Extension of Scope of Reactions

Various expedients have been devised to overcome the limitation to the scope and general usefulness of electro-organic reactions, imposed by the low solubility of many organic substances in aqueous electrolytes. Frequently the solubility of the depolarizer is increased by the addition to the aqueous electrolyte of a water-miscible liquid, such as alcohol, acetone, or glacial acetic acid, in which the depolarizer is soluble. This procedure has, however, the disadvantages of increasing electrolytic resistance and of introducing a substance which may act as a depolarizer and so decrease the yield of desired product. These disadvantages may be eliminated partially, if not entirely, by the use of sodium salts of organic acids of high molecular weight as the depolarizer solvent. Such solvent solutions, in which many organic substances are readily soluble, are not only good conductors but they do not act as cathodic depolarizers. Solvent solutions of this type have been used successfully for the electrolytic reduction of aromatic nitrocompounds (29).

Depolarizers of limited solubility may be brought into contact with the electrode as suspensions or emulsions in the aqueous electrolyte, the latter being maintained either by mechanical means or by the use of an emulsifying agent (27, 30). Due to a wick action which transports the depolarizer to its active surface, a porous electrode has proved effective in the reduction of insoluble liquid depolarizers. In this manner nitrobenzene, for example, has been reduced at a porous carbon electrode in contact with an aqueous electrolyte and the nitrobenzene (31). In reactions for which carbon is unsuitable as the electrode material, "wicking-electrodes" may be prepared by coating porous carbon with an appropriate metal.

The electrolytic oxidation or reduction of a solid insoluble depolarizer may be accomplished by introducing it into the electrode. This expedient has been employed with success for the oxidation of anthracene, by employing as the anode a storage battery grid into the slots of which is pressed a paste composed of the depolarizer, lead dioxide, and sulfuric acid (32).

Commercial Applications

Notwithstanding the large number of organic compounds that has been prepared by electrolytic methods in the laboratory, only a few electro-organic reactions have been carried out on a technical scale.

The commercial purification of *n*-butyl alcohol has been achieved in the cathode section of an electrolysis cell (33). A continuous, commercially feasible operation has been developed for the electrolytic reduction of acetone to pinacol for subsequent conversion into 2,3-dimethyl butadiene (34). The electrolytic manufacture of *p*-amidophenol and benzidine is in operation at several plants in Europe and was, at one time, in use in this country; and it is probable that the electrolytic reduction of fumaric acid to succinic acid (35) is being employed to an increasing extent, and that by this means pyridine is transformed to piperidine (36). Gluconic acid has been produced in commercial quantities by the electrolytic oxidation of glucose (37). Millions of pounds of mannitol and sorbitol have been manufactured by the electrolytic reduction of glucose at a plant which started operation in 1937, with a monthly capacity of 250,000 pounds of these hexatols. This electrolytic process and the plant have been described (38) and the performance of the electrolysis cells discussed (39). A recent commercial application of electro-organic chemistry is the electrolytic fluorination of organic compounds, which is being carried out in this country on a pilot plant scale (40).

Among the handicaps responsible for the very limited application of electro-organic syntheses on a commercial scale, the following are frequently cited: (*a*) low cell capacity due to the slow rate of depolarization and, consequently, the large floor space required; (*b*) the limitations resulting from the low solubility of many organic substances in aqueous electrolytes; (*c*) the high costs of electrical energy; (*d*) the necessity for careful control; and (*e*) the complexity and expense of equipment. Procedures for overcoming the first two, at least partially, have already been indicated; the last two handicaps are, perhaps, inherent.

The energy costs of the electrolytic production of many organic compounds compare favorably with those of other methods. In the case of electrolytic oxidation there is a good margin and in that of electrolytic reduction a fair one, except when the cheapest reducing agents, such as iron (41) and hydrogen, are involved. A material decrease in energy costs and possibly, therefore, a stimulation of the technical application of electro-organic chemistry would result, if it were possible to carry out simultaneously and successfully, in the same cell, desirable oxidation and reduction reactions. While such a development is important (42), up to the present time but few oxidations and reductions have been effected in the same cell at the same time. The oxidation of anthracene to anthraquinone and the reduction of azobenzene to benzidine have been achieved, with good yields, in a cell of commercial size (43). Single cells have also been used for the simultaneous production of *p*-amidophenol and ammonium persulfate (44) and of hexatol and lead dioxide (45).

In the selection of electro-organic syntheses that might lend themselves to commercial development, a recent, critical compilation of published electro-organic reactions should prove of value. This significant bibliography lists only those reactions which give yields equal or superior to those obtained by purely chemical methods (46).

REFERENCES

1. G. A. Roush, *Trans. Electrochem. Soc.*, **8**, 281 (1905).
2. *Met. and Chem. Eng.*, **13**, 211 (1915).
3. F. Haber, *Z. Elektrochem.*, **4**, 506 (1898).
4. J. Tafel, *Z. physik. Chem.*, **34**, 187 (1900); W. Löb and R. W. Moore, *ibid.*, **47**, 418 (1904).
5. A. Hickling, *Trans. Faraday Soc.*, **38**, 27 (1942).
6. J. Tafel, *loc. cit.*, and *Ber.*, **33**, 2209 (1900).
7. H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939); E. A. Parker and S. Swann, Jr., *ibid.*, **92**, 348 (1947).
8. S. Swann, Jr., and J. Feldman, *Trans. Electrochem. Soc.*, **67**, 195 (1935).
9. S. Swann, Jr., *Trans. Electrochem. Soc.*, **64**, 313 (1933).
10. S. Swann, Jr., L. F. Deditius, and W. A. Pyhrr, *Trans. Electrochem. Soc.*, **68**, 321 (1935).

11. C. L. Wilson, *Trans. Electrochem. Soc.*, **75**, 357 (1939).
12. S. Glasstone, *Trans. Electrochem. Soc.*, **75**, 410 (1939).
13. H. R. Neumark, *Trans. Electrochem. Soc.*, **92**, 389 (1947).
14. O. C. Slotterbeck, *Trans. Electrochem. Soc.*, **92**, 377 (1947); cf. S. Swann, Jr., *ibid.*, **63**, 239 (1932).
15. S. Swann, Jr., and coworkers, *Trans. Electrochem. Soc.*, **75**, 411 (1939); **80**, 163 (1941); **84**, 165 (1943); **85**, 231 (1944); **96**, 353 (1949).
16. S. Swann, Jr., and H. J. Read, *Trans. Electrochem. Soc.*, **69**, 345 (1936).
17. H. J. Read, *Trans. Electrochem. Soc.*, **80**, 133 (1941).
18. E. A. Parker and S. Swann, Jr., *Trans. Electrochem. Soc.*, **92**, 348 (1947).
19. D. N. Solanki, *Trans. Electrochem. Chem.*, **88**, 97 (1945).
20. E. Isaacs and C. L. Wilson, *J. Chem. Soc.*, **1936**, 202.
21. W. G. Albert and A. Lowy, *Trans. Electrochem. Soc.*, **75**, 371 (1939); S. Swann, Jr., and G. D. Lucker, *ibid.*, **75**, 411 (1939).
22. H. J. Creighton and R. A. Hales, U. S. Pat. 2,458,895, Jan. 11, 1949.
23. F. Haber and A. Moser, "Elektrolytischen Prozesse der organischen Chemie," p. 108, Wilhelm Knapp, Halle, Germany (1910).
24. W. Löb, *Z. Elektrochem.*, **8**, 778 (1902).
25. E. Tommila, *Suomen Kemistilehti*, **9**, 76 (1936).
26. S. Glasstone, *Trans. Faraday Soc.*, **19**, 574 (1924).
27. S. Glasstone and H. E. Stanley, *Trans. Electrochem. Soc.*, **92**, 327 (1947).
28. Cf. R. W. Mitchell, *Trans. Electrochem. Soc.*, **56**, 495 (1929); R. H. McKee and J. R. Heard, *ibid.*, **65**, 301 (1934); R. W. Lewis and O. W. Brown, *ibid.*, **84**, 135 (1943).
29. R. H. McKee and C. J. Brockman, *Trans. Electrochem. Soc.*, **62**, 203 (1932); R. H. McKee and B. G. Geraposto-lou, *ibid.*, **68**, 329 (1935).
30. R. W. Mitchell, Reference 28.
31. N. M. Winslow, *Trans. Electrochem. Soc.*, **88**, 81 (1945).
32. C. H. Rasch and A. Lowy, *Trans. Electrochem. Soc.*, **56**, 477 (1929); E. G. White and A. Lowy, *ibid.*, **62**, 229 (1932).
33. R. S. W. Rowell and Imperial Chemical Industries, British Pat. 335,638, Oct. 20, 1929.
34. O. C. Slotterbeck, U. S. Pat. 2,408,10f, Sept. 24, 1946; Reference 14.
35. J. F. Norris and E. O. Cummings, U. S. Pat. 1,457,791, June 5, 1923.
36. M. deK. Thompson, Theoretical and Applied Electrochemistry, pp. 286–7, The Macmillan Co., New York (1939).
37. C. G. Fink and D. B. Summers, *Trans. Electrochem. Soc.*, **74**, 625 (1938).
38. H. J. Creighton, U. S. Patents 1,612,361, Dec. 28, 1926; 1,990,582, Feb. 12, 1935; *Can. Chem. Process Inds.*, **28**, 690 (1943); see also Reference 8; D. H. Killeffer, *Ind. Eng. Chem. News Ed.*, **15**, 489 (1937); R. L. Taylor, *Chem. Eng.*, **44**, 588 (1937).
39. M. T. Sanders and R. A. Hales, *J.* (*and Trans.*) *Electrochem. Soc.*, **96**, 241 (1949).
40. J. H. Simons *et al.*, *J.* (*and Trans.*) *Electrochem. Soc.*, **95**, 47 (1949); J. H. Simons, U. S. Pat. 2,519,983, Aug. 22, 1950.
41. F. A. Lidbury, *Met. and Chem. Eng.*, **13**, 211 (1915).
42. W. D. Bancroft, *Trans. Electrochem. Soc.*, **36**, 348 (1919); F. C. Frary, *ibid.*, **45**, 104 (1924); C. G. Fink, *ibid.*, **50**, 348 (1926).
43. C. J. Thatcher, U. S. Pat. 1,544,357, June 30, 1925; *Trans. Electrochem. Soc.*, **51**, 181 (1927).
44. A. S. McDaniel *et al.*, *Trans. Electrochem. Soc.*, **39**, 441 (1921).
45. H. J. Creighton, Unpublished results.
46. S. Swann, Jr., *Trans. Electrochem. Soc.*, **69**, 287 (1936); **77**, 459 (1940); **88**, 103 (1945); cf. *Univ. Illinois Eng. Exp. Sta., Circ. Ser. No. 50 (1948).*

ORGANIC POLAROGRAPHY

*Stanley Wawzonek**

The general field of polarography may be divided into two subdivisions: (*a*) the study of inorganic compounds in aqueous solutions, and (*b*) the study of organic compounds in various media. The field of organic polarography, or micro electroorganic chemistry, has seen a slower development than its inorganic counterpart because of the inherent nature of organic compounds. Their insolubility in water requires studies to be made in mixtures of water with organic solvents or in nonaqueous media. Because of their unsaturation the electrode reactions involve hydrogen ions and make the use of buffered solutions desirable. Moreover, the electrode reactions are difficult to formulate since the majority of the reductions and oxidations of organic compounds are irreversible and the nature of the products is often unknown. In spite of these difficulties, over 600 papers have been published on the subject with the majority of them appearing in the last ten years. This field has been intimately associated with The Electrochemical Society from its earliest days and a number of papers have been presented at the meetings and published in the JOURNAL.

This science up to the present time has dealt mainly with the theory and applications of the dropping mercury electrode in mixtures of water and organic solvents. Of necessity the studies have been limited to compounds which are soluble and stable toward hydrolysis in such media. The applied field has been concerned with (*a*) the qualitative detection and quantitative determination of organic compounds, (*b*) structural determination, (*c*) the relation between structure and half-wave potentials, and (*d*) the mechanism of electroreductions. The analytical use has been applied to the study of the kinetics of reactions and to determine the extent of completion of a reaction in which one or more of the reactants or the reaction products are reducible at the dropping mercury electrode. A minor use, but one which has future possibilities, is the determination of conditions polarographically for the large scale electrolytic preparation and chemical preparation of organic compounds. The use of solid electrodes in polarography may become important in this respect.

Polarography saw its beginning in the first publication by Jaroslav Heyrovsky in *Chemické Listy*, **16,** 256 (1922) and later on more completely in the *Philosophical Magazine*, **45,** 303 (1923) on the phenomena displayed in electrolysis with the dropping mercury electrode. This work which involved a study of the deposition of alkali and alkaline earth metals was quickly followed in the next year by the electroreduction of the first organic compound, nitrobenzene, by Shikata, a young Japanese coworker of Heyrovsky's. The results on this compound were not published until 1925 although the paper was presented before the Faraday Society in 1923.

Work in the organic field was continued by Shikata and his students in Japan and extended to the reduction of aliphatic aldehydes and ketones, pyridines, substituted aromatic nitrocompounds and azobenzenes. Comparisons were made in these investigations between the reduction-potentials and structures, which later (1938) evolved into the Shikata's electronegativity rule of the reduction potentials of organic compounds.

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In Czechoslovakia, Heyrovsky and his students, Herasymenko, Smoler, and Schwaer, continued work on organic compounds and studied the reduction of acetaldehyde, sugars, oxalic acid, fumaric, maleic, and other unsaturated acids. They were joined in this field in 1932 by Semerano in Italy who published on the reduction of aromatic aldehydes. This period also saw the first use of the dropping mercury electrode as an anode in the oxidation of hydroquinone (1934) and the placing of polarography upon a more scientific basis. Experience up to this time had shown that the limiting current was proportional to the concentration of the reducible substance under identical conditions. The development of the Ilkovic equation in which the limiting or diffusion current is shown to be related to the concentration and diffusion coefficient of the substance and the capillary characteristics occurred in 1934. The demonstration by Heyrovsky and Ilkovic in 1935 that the half-wave potential was independent of the concentration and rate of flow of mercury was also of fundamental importance.

It was not until 1937 that polarography actually took on more of an international aspect. The main reason for this change was no doubt Heyrovsky's lectures on polarography as Carnegie Visiting Professor in 1933 at the University of California at Berkeley, Stanford University, California Institute of Technology, various midwestern and eastern universities in the United States, and at the Radium Institute in Leningrad on the occasion of Mendeleev's Centenary Celebration (1934) in Russia. These lectures were aided in publicizing the method somewhat by the appearance of a book by Heyrovsky on Polarography in 1933 in Czechoslovakian and the recognition given to the method by the extending of an invitation to Heyrovsky to write an article for Böttger's Volume II of his "Physikalische Methoden der analytischen Chemie" in 1936.

The first papers published in this country were on applications of the method to the solving of organic chemical problems. Jurs and Noller in 1936 used the method to detect and estimate the amount of fructose present in the hydrolysis products of a saponin. This work was quickly followed by a demonstration (by Borcherdt, Meloche, and Adkins in 1937) that the method could be used to measure amounts of ketones in the presence of each other. These investigators then proceeded to use the method to study the tautomerization of an optically active azomethine (1938) and to establish the relative oxidation-reduction reactivities of ketones and aldehydes (1938). Lauer, Klug, and Harrison are credited with the first use of this method for structure determination in 1939. The behavior of the green α- and red β-*p*-azophenols at the dropping mercury electrode was found to be identical and indicated, in agreement with x-ray studies, that the compounds were not cis-trans isomers.

The year 1937 also marked the beginning of work on theoretical polarography in this country by O. H. Müller who demonstrated that the half-wave potential for a reversible oxidation-reduction system (quinones) corresponded to the standard electrode potential for this system. These important results were presented at the 71st general meeting of The Electrochemical Society in Philadelphia on April 29, 1937 and represented the first of a number of investigations upon

polarography which have been presented before this organization and which have appeared in the JOURNAL of the Society.

In Europe, extension of the method occurred at about the same time as in the United States. The first paper from Germany by Winkel and Proske on the reduction of a variety of carbonyl compounds appeared in 1936. The first contribution from France by Hoang on azo dyes was published in 1938 while that from England on phenyl alkyl ketones by Davies occurred in 1939. In the same year (1939) Neiman in Russia published his first paper on peroxides.

Probably the greatest stimulation to polarographic studies was given by the appearance of review articles on polarography by Kolthoff and Lingane, and by Müller in 1939, and of books on polarography by Kolthoff and Lingane (1941) in this country, and by Heyrovsky (1941) in Europe. The latter book was a revision of his first edition and was written in German. These treatises had a great effect upon polarography since they pointed out the errors of the past and stressed the use of half-wave potentials, buffered solutions, and other standardized procedures for future work. These recommendations have been followed by the majority of polarographers.

The period following the publication of these books has seen a voluminous increase in the papers on organic polarography. Only brief mention can be made of some of these which expanded or contributed to the understanding of the subject.

Some of the most important papers were those by Brdicka (1941) on the interpretation of adsorption waves. This phenomenon changed the behavior of some reversible systems from that observed potentiometrically by introducing a small anomalous reduction wave before the main reduction step.

The same investigator (1937) was also instrumental in the discovery of kinetic currents which are important in the polarographic behavior of compounds that exist in equilibrium with closely related structures. Common examples are formaldehyde and its hydrate, aldohexoses and their cyclic structures, and acids in which reducible groups are present and their anions.

Numerous groups and structures were added to the list of polarographically reducible and oxidizable possibilities. The behavior of the mercaptan-disulfide system as present in cysteine-cystine, arsonic acids, and chromans and coumarans at the dropping mercury electrode has been reported on by Kolthoff and his coworkers. The reduction of aromatic unsaturated hydrocarbons and polynuclear aromatic hydrocarbons was demonstrated by Laitinen and Wawzonek (1942), aliphatic dienes and organic halogen compounds by von Stackelberg and Stracke (1949), phenylmercuric salts by Benesch (1951), diazonium salts by Atkinson (1950), various oxygen heterocyclic compounds by Geissmann (1949), Santavy and others (1950), pyridines by Tompkins (1943), quinoline by Knobloch (1947), substituted quinolines by Stock (1944), and acridines by Kay and Stonehill (1951). The work of Pearson (1948) on aromatic nitrocompounds contributed greatly to the understanding of the polarographic behavior of these possibilities while that of Petru (1947) elucidated the steps in the reduction of the aliphatic compounds.

The work on diazonium salts stimulated the use of the cathode ray polarograph in organic analysis and in the reaction kinetic field where quick determinations are necessary. Thus, accurate results have been obtained in the analysis of formaldehyde in slightly basic solutions in the presence of acetone. This analysis has to be performed quickly because formaldehyde and acetone condense rapidly in basic me to β-hydroxyethyl methyl ketone. The instrument can used to follow a fast reaction such as the coupling of a azonium salt with a coupler which is completed in the ra of thirty to one hundred and fifty seconds.

The possibility of using the polarographic method as pilot technique to establish optimum electrolysis conditio of electrolyte and cathode potential was first suggested Lingane (1943) and demonstrated by the successful prepar tion of 9-(*o*-iodophenyl)dihydroacridine from 9-(*o*-iodopheny acridine using a large mercury cathode and efficient stirri All chemical reducing agents tried either did not effe reduction or led to complete reduction to 9-phenyldihydr acridine. The electrolytic reduction was carried out at constant potential which corresponded to the value at whi the first diffusion current plateau was reached at the dro ping mercury electrode. This technique has been widely us in establishing the mechanism of reduction of organic co pounds at the dropping electrode by producing enough the product so that it can be isolated and identified. T process has apparently been tried only once for a large sca preparation of an organic compound (pinacol from *p*-amin acetophenone) and found to yield only *p*-aminophenylmethy carbinol. This behavior indicates that polarographic da alone are not sufficient to predict the products at a lar mercury electrode with stirring. It must be remembered th at the dropping mercury electrode only diffusion proces are involved. Intermediates are therefore not removed fro the electrode surface, as in the large scale stirred preparati to the solution where dimerization, disproportionation, rearrangement can occur. A factor which has to be co sidered in varying the amounts of these side reactions in t large scale process apparently is current density.

The use of polarographic data as an aid in predict chemical reduction has been carried out by Ochiai (19 in his work with 4-nitropyridine-N-oxide and 4-nitroquinoli N-oxide. The polarographic reduction potentials for t nitro and N-oxide groups differed from each other by mo than one volt and indicated that the former could be r duced more easily than the latter. This fact was confirmed b the excellent yields of the corresponding amino-N-oxid using chemical reducing agents.

The use of solid electrodes in polarography has been co fined mainly to studies of reversible systems and oxidati reactions with the microplatinum electrode. The only e ample studied at other metallic electrodes was the reducti of nitrobenzene (1949) at spherical copper, silver, and am gam electrodes; curves similar in shape to those formed at t dropping mercury electrode were obtained. This techniq may become more important in the future in establish conditions for the reduction of organic compounds at so electrodes.

Polarographic studies in nonaqueous media have be limited thus far mainly to solvents with hydroxyl group e.g., alcohols, glycerol, ethylene glycol, methyl cellosol and acetic acid. These liquids have the same disadvanta as aqueous mixtures toward easily hydrolyzable compound Media which do not have the hydroxyl grouping either ha been used only to a limited extent (formamide) or have to low a dielectric constant and will dissolve very little ine electrolyte (benzene, toluene, and aniline). This field wit out doubt will be investigated more intensely in the future.

Feature Section

The Electrolytic Polishing of Lead-Tin Alloys for Microscopic Examination

*A. W. Moulen**

Introduction

The technique for the electrolytic polishing of lead, tin, and their alloys, described below, produces polished and etched specimens without laborious initial grinding and surface preparation, at the same time avoiding the handling of potentially explosive chemicals.

Lead and tin have been polished electrolytically by Jacquet (1) using perchloric acid-acetic anhydride electrolytes, while de Decker, Krijff, and Pluut (2) have described conditions for polishing lead-tin alloys in a dilute perchloric acid-ethyl alcohol electrolyte. Perchloric acid is potentially explosive when in contact with organic materials and with bismuth and its alloys. The evolved method required only a small degree of bath composition control with a safe inexpensive electrolyte, used over a wide range of both bath temperatures and anode current densities.

Experimental

Specimens used ranged from commercially pure tin through various lead-tin alloys, as shown in Table I. Specimens were

TABLE I

Specimen No.	Composition		Fig. No.
	% Pb	% Sn	
	by weight		
1	—	100	3
2	10	90	4
3	38	62	5
4	80	20	6
5	95	5	7
6	100	—	8

chill cast in a simple flat bottom brass mould to produce a button of metal about one inch in diameter. On cooling, the surface of the specimen was carefully turned on a lathe to give a surface as illustrated in Fig. 1, about $\frac{1}{16}$ in. (1.6 mm) being removed from the specimen surface to assure penetration of the skin of the casting.

Apart from the specimen being rinsed with alcohol and dried after turning, no other surface treatment was given before the polishing procedure was begun.

Apparatus

Electrolytic polishing was first attempted in a glass beaker using a range of concentrations of aqueous fluoboric acid solutions. In some cases, lead was polished to a highly lustrous surface finish, but considerable difficulty was incurred in removing the specimen from the electrolyte without severely etching the surface or causing a fine "bloom" to form on the newly polished surface. If either the current was cut off

FIG. 1. Tool marks on a turned lead-tin alloy specimen. 100×.

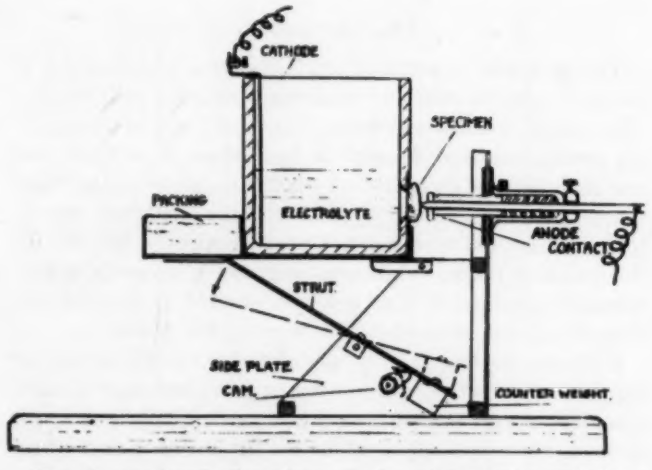

FIG. 2. Sectional elevation of the electrolytic polishing cell.

before the specimen was removed from the electrolyte or the specimen was removed while the current was flowing, a deterioration of the surface finish resulted.

To overcome etching the specimen during removal from the electrolyte, a modification of the inclinable cell designed by Parcel (3) was built. This is illustrated in Fig. 2.

The brass cell holder was coated with a polyvinyl chloride

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lacquer to prevent corrosion. It was fitted with an adjustable spring-loaded anode contact which held the specimen against an aperture in the side of a hard rubber cell made from a two-volt lead accumulator case.

The cell could be maintained in either an inclined or horizontal position. While in the inclined position, the electrolyte was poured into the rubber cell up to the level of the anode aperture. After the specimen was placed over the aperture in the cell wall, the cell was raised to the horizontal position, the level of the electrolyte in the cell rising above the specimen and electrical contact being made by the spring-loaded anode holder. The cell was designed so as to make or break the electrical circuit as rapidly as possible.

The frame holding the rubber cell was supported by a pivoted brass strut. This strut was counterweighted so that when free it rested at 45° to the horizontal. The pressure of a lever-operated cam sprung the supporting strut sufficiently to rotate it after a slight upward movement of the cell and supporting frame. The cell and supporting frame could then be lowered rapidly to the inclined position at the same time as the specimen was removed from contact with the electrolyte.

A simple series circuit was used to control the current, supplied to the electropolishing cell by a bank of lead accumulators.

The cathode consisted of a piece of 18 gauge 18-8 stainless steel 1¼ in. (4.8 cm) wide, of which an area of 1¼ in. (4.8 cm) x 2½ in. (6.4 cm) was exposed to the anode when the cell was in operation. The cathode could be fitted at various distances from the anode aperture. The inside dimensions of the cell were 1¼ in. (4.8 cm) wide, 4¼ in. (10.5 cm) long. The anode aperture was set at 1¼ in. (2.9 cm) from the bottom of the inside of the rubber cell, and was bored to have an area of one-third of a square inch to facilitate current density calculations. The inside of the aperture was champhered at 45° to allow precipitated salts to fall freely away from the vicinity of the anode while electropolishing was in progress.

The Electrolyte

The bath was commercial grade fluoboric acid, being a 40 per cent aqueous solution containing 2 per cent sulfuric acid. The sulfuric acid did not play an important part in the polishing mechanism, since electrolyte from which the sulfuric acid was removed, by precipitation with barium carbonate, functioned quite satisfactorily. With sulfuric acid-free electrolytes, voltage and current densities were slightly different for the polishing range. While polishing was in progress, a considerable quantity of hydrogen was evolved at the cathode, there being no visible evolution of gas at the anode.

With tin, a white to gray sludge formed at the anode for low current densities, whereas in the polishing range a black film formed over the surface of the anode. With lead specimens, a white film appeared on the surface of the specimen and, in baths containing sulfuric acid, some of the lead was precipitated as lead sulfate. This precipitate did not interfere with the polishing action. The bath appeared to be fairly stable, since, after fifty polishings no marked deterioration had occurred in 250 cc of electrolyte. While polishing was in operation on lead, tin, and their alloys, a spongy deposit of lead and tin was formed on the cathode.

Polishing Technique

The specimens, after turning and rinsing with alcohol, were dried and placed over the anode aperture while the cell was in the inclined position. On elevating the cell to the horizontal position, contact of the specimen with the electrolyte and the spring-loaded anode started the current flowing. The range of cell voltages and current densities for polishing lead-tin specimens is given in Table II.

TABLE II

Specimen Fig. No.	Composition		Current density		Cell voltage, volts	Temp °C	Time, min
	% Pb	% Sn	Amp/in.²	Amp/cm²			
3	—	100	27–36	(4.2–5.6)	15–17	20–37	3–5
4	10	90	30–45	(4.7–7.0)	16–20	20–45	3–5
5	38	62	35–45	(5.4–7.0)	16–20	20–45	3–5
6	80	20	35–45	(5.4–7.0)	16–20	20–45	3–5
7	95	5	35–45	(5.4–7.0)	16–20	20–45	3–5
8*	100	—	24–45	(3.7–7.0)	16–21	20–40	3–5

* For pure lead, a longer polishing time could be employed if the electrolyte were agitated.

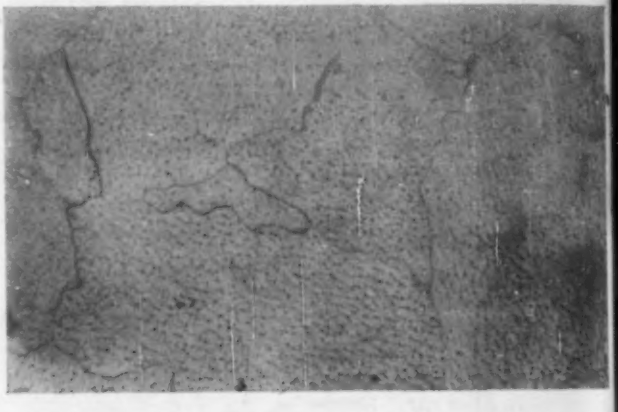


FIG. 3. Tin 100×. The mosaic structure inside the crystal boundaries is due to small quantities of impurity in the tin.

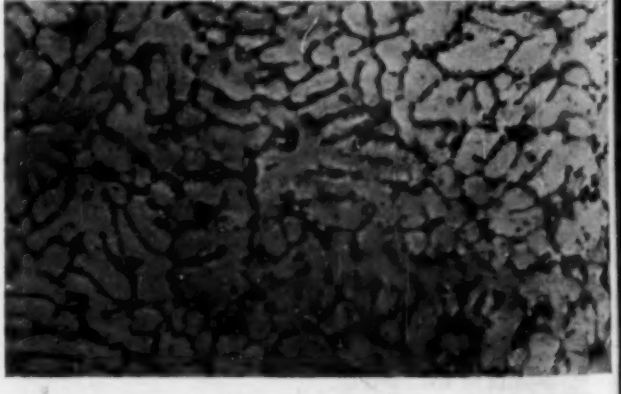


FIG. 4. Alloy of 90% tin with 10% lead, showing tin-rich solid solution and lead-rich solid solution precipitated from the tin-rich solid solution during cooling. 250×.

After the contact was made, the current flowing through the cell fell off rapidly as a film was formed on the anode

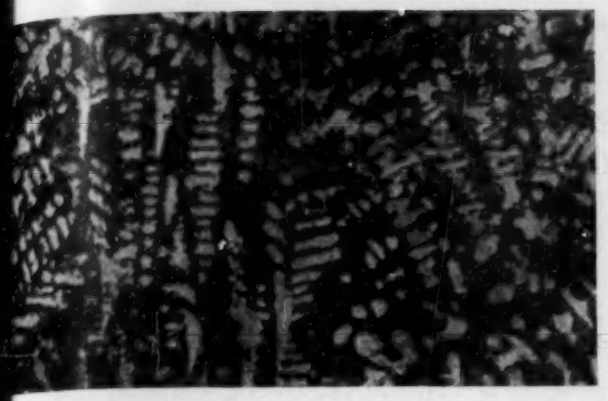


FIG. 5. Alloy of 62% tin with 38% lead, showing a eutectic mixture (dark) and tin-rich solid solution. The tin-rich component is present as a dendritic formation. 250×.

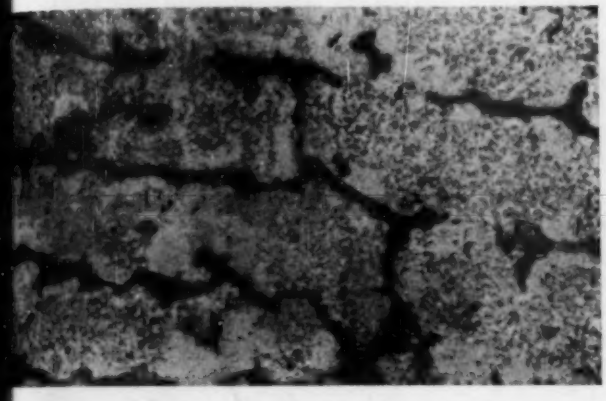


FIG. 6. Alloy of 20% tin with 80% lead showing lead-rich solid solution (white), areas of precipitated tin-rich solid solution and dark areas of dense eutectic. 250×.

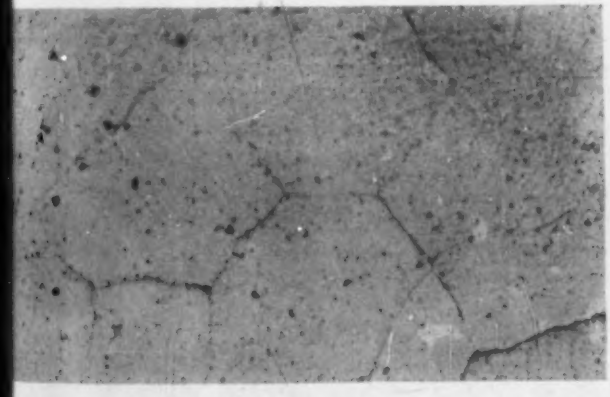


FIG. 7. Alloy of 5% tin with 95% lead, showing lead-rich solid solution grains, with finely divided tin-rich solid solution precipitation dispersed through the grains. 250×.

surface. If the specimen were removed from the cell when the current had fallen to a stable value, the film on the anode surface was loosely adherent, and could be washed from the specimen leaving a surface which when examined under the microscope revealed the structure of the alloy treated. The photomicrographs, Fig. 3–8, were photographed directly after polishing and etching in this manner, the specimen having been first washed in running water, rinsed, and dried.

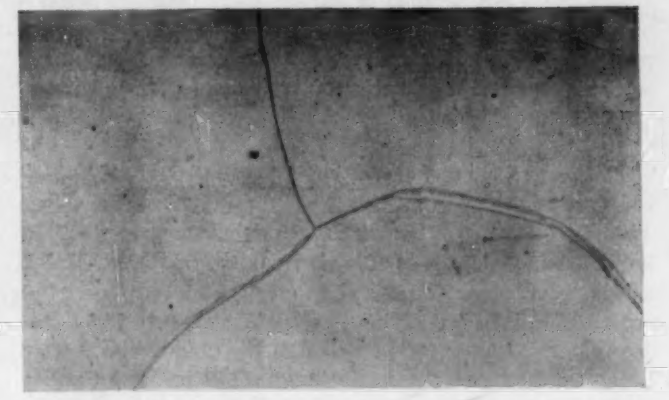


FIG. 8. Pure lead showing grain boundaries and inclusions. 250×.

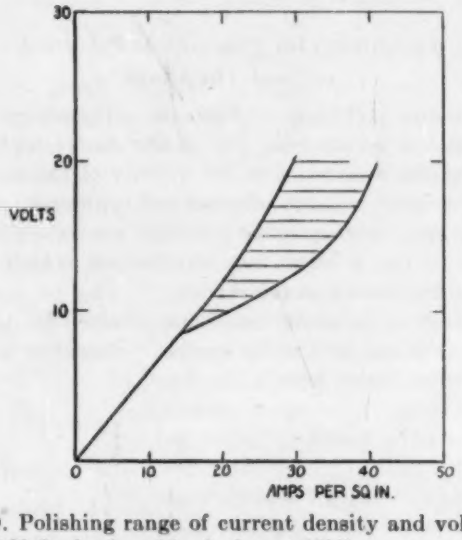


FIG. 9. Polishing range of current density and voltage for lead in 40% fluoboric acid solution at 25°C.

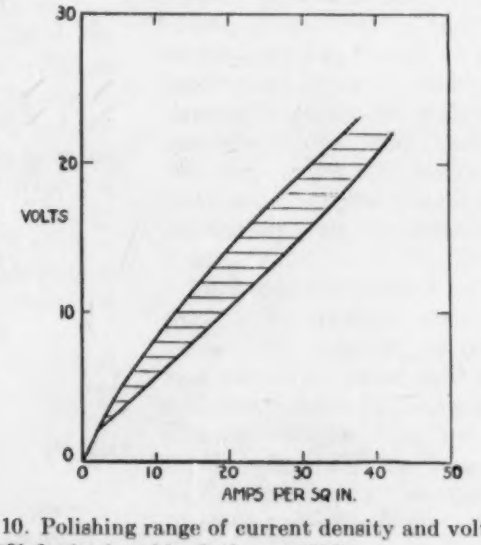


FIG. 10. Polishing range of current density and voltage for tin in 40% fluoboric acid solution at 25°C.

If the specimen were allowed to remain in contact with the electrolyte after the current had fallen to its lower value, the current caused local heating of the electrolyte and severe

corrosion of the metal surface. In general, the electrolytic action could not be maintained for more than ten seconds owing to heating of the specimen and electrolyte. Repeat polishes could be used if the tool marks were not completely removed from the surface of the specimen in one operation.

Results

The photographs, Fig. 3–8, of the metals and alloys polished, reveal the expected structures of cast lead-tin alloys. The mosaic structure inside the crystal boundaries (Fig. 3) is due to small quantities of impurity in the tin. C. W. Mason and W. G. Forgeng (4) reported that pure tin to which 0.004 per cent bismuth had been added had a structure which was deceptively like a eutectic, although the quantity of foreign metal was far below the limit of solid solubility. Fig. 5 shows small particles of the anode film which have adhered to the specimen surface. In the case of lead (Fig. 8), the specimens showed inclusions around which no marked corrosion had occurred.

Conditions for Electrolytic Polishing of Lead-Tin Alloys

Electrolytic polishing in fluoboric acid solution (either commercial or sulfate free) was, in the case of lead, accompanied by the occurrence in the vicinity of the anode of a white film which was not adherent and continually streamed from the anode surface while polishing was in operation. In the case of tin, a black film was formed, which adhered loosely to the surface of the anode.

The range of polishing conditions obtained for pure lead and tin when current density against voltage was plotted is shown by the shaded areas in Fig. 9 and 10.

Conclusion

The method of preparing lead-tin alloys for microscop examination described in this paper avoids the time-consum ing initial preparation of these soft alloys, and involves n great skill in manipulation.

It is probable that investigation of the polishing behavio on zinc, copper alloys, and some alloy steels in fluoboric ac based electrolytes may lead to further advancement in th laboratory electropolishing field.

Acknowledgments

The author is indebted to Professor T. G. Hunter (De partment of Chemical Engineering, University of Sydney for his interest and encouragement, to Mr. H. S. Parker fo his assistance in the design and fabrication of the inclinab cell, and to Mr. J. N. Ellis for his assistance in photographin the microstructures.

Thanks are also due to The Electrochemical Society fo their financial assistance through the Roeber Research Fun and to the Commonwealth Research Fund (Australia) fo their financial aid.

REFERENCES

1. P. A. Jacquet, *Rev. mét.*, **37**, 210 (1940).
2. H. E. J. de Decker, A. P. Krijff, and J. M. Pluut, *Sh Metal Inds.*, **24**, 2235 (1947).
3. R. Parcel, *Metal Progress*, **42**, 209 (1942).
4. C. W. Mason and W. C. Forgeng, *Metals & Alloys*, **6**, (1935).

Current Affairs

Activities of Local Sections: New Officers Elected

Cleveland Section

The March 8 meeting of the Cleveland Section was designated as "Local Talent Night" and designed as an experiment in local section activities. Instead of bringing a noted speaker into town, a program was arranged to give young electrochemists, all residing in the Cleveland area, the opportunity to present some of their own original research before the Section.

The purpose was also to see whether a program of this kind would provide high caliber technical presentations, whether it would interest the Section membership, and whether it would attract more young electrochemists and guests to the meeting. From all points of view, the experiment turned out to be a great success. It drew the largest attendance of the season, the presentations were all excellent, and the subjects were sufficiently diversified to keep all of the audience interested throughout the evening.

Each speaker was allotted 15 to 20 minutes for his presentation, after which some time was allowed for discussions. The speakers and subjects were as follows:

L. R. Shiozawa, Case Institute of Technology, "The Electrochemical Behavior of Zinc and Galvanized Steel in Aqueous Solutions"

C. I. Hildreth, National Carbon Company, "Applications of the Theory of Electrolytes to Practical Problems"

E. B. Yeager, Western Reserve University, "Applications of Ultrasonics to Electrochemistry"

Judging from the success of this meeting, similar activities can be highly recommended to other local sections of the Society.

H. C. Froelich, *Chairman*

Midland Section

The feature of the April 1 meeting of the Midland Section, held at the Dow Auditorium, Midland, was the showing of the film "Corrosion in Action." This is an educational motion picture in color produced by the International Nickel Company (described in the May Journal under the New York Section meeting).

Dr. T. P. May, of the International Nickel Company, who had done considerable work in the preparation of the film, introduced the subject and described some of the production difficulties encountered in its preparation. Following the presentation there was further discussion of the filming of various scenes. It was a very interesting meeting, attended by about 175 Dow personnel.

W. R. Perry, *Secretary*

Niagara Falls Section

The Niagara Falls Section held its annual Ladies' Night meeting at the Red Coach Inn on April 16.

Gardner H. Dales, Special Studies Engineer of Niagara Mohawk Power Corporation, spoke on the topic "More Power From Niagara." The history of Niagara's power development, and the engineering and political aspects of the contemplated further use of Niagara's power potential were very well presented. The subject, which is of close concern to the members of this section, brought out a very active discussion at the conclusion of the talk.

At the business meeting the following officers were elected for the year 1952–53:

Chairman—Morton S. Kircher, Hooker Electrochemical Company

Vice-Chairman—Harry R. Oswald, Oldbury Electro-Chemical Company

Secretary-Treasurer—Milton Janes, National Carbon Company

Harry R. Oswald, *Vice-Chairman*

Pittsburgh Section

The Pittsburgh Section met on February 27 at the Mellon Institute. J. M. Guthrie, Chairman of the local section, introduced the guest speaker for the evening, Howard T. Francis of the Armour Research Foundation, Illinois Institute of Technology, Chicago, Illinois.

Dr. Francis described a new method for the mapping of potential fields surrounding a corroding specimen. The technique is known as "the rotogenerative method," and was developed in connection with a project sponsored by the National Advisory Committee for Aeronautics.

A cylindrical specimen is employed, which is rotated in the corrosion medium at several hundred rpm. One or more "scanning electrodes" are positioned near the specimen surface and serve to detect variations in the electrostatic field which rotates with the corrosion specimen. The reference electrodes are 5 mil silver wires, imbedded in an insulating plastic and exposed in cross section. The voltage variations detected by the reference electrode are amplified as an a-c signal and viewed on an oscilloscope. The standing patterns so produced show upward and downward "pips," which accurately reflect the position and approximate magnitude of the local anodes and cathodes on the corroding specimen.

An alternative method of scanning employs 24 scanning electrodes and presents the signal on an oscilloscope as a series of horizontal lines, much as a television picture. The anodic and cathodic voltages from the scanning electrodes modulate the intensity of the oscilloscope beam, thus producing a black and white "picture" of the corroding metal surface. Anodes and cathodes appear as dark and light regions, respectively.

Although the development of the apparatus is not yet complete, initial results indicate that the technique should be applicable to a number of corrosion problems, including inhibitor action, cathodic protection, and pos-

sibly electrodeposition studies.

At the conclusion of the address, a very lively discussion ensued in which many new potential applications of this method and their ramifications were discussed.

R. D. WILLIAMS, *Secretary-Treasurer*

Washington-Baltimore Section

Thomas D. Callinan and Van A. Wente of the Naval Research Laboratory, Washington, D. C., described new types of electrical insulating materials at the meeting of the Section held on April 17, at the National Bureau of Standards.

Mr. Callinan, the first speaker, described the properties and preparation of papers made from asbestos and mica, glass, silica, and ceramic fibers. After acknowledging the fine cooperation of the late Bourdon W. Scribner and his staff at the National Bureau of Standards for their part in making experimental runs on papers made from the above fibers, Mr. Callinan outlined briefly the experimental work which has led to various stages of development of electrical insulating papers made from the basic materials referred to above.

Two general approaches were made in this attempt to improve high temperature performance of electrical insulating papers. The first was directed toward an effort to make use of inorganic materials such as asbestos, bentonite, and mica, and the second toward the production of fine inorganic fibers of glass, ceramic, and silica.

The work on asbestos involved a method of separation of magnetite from the asbestos in Canadian crysotile by means of a Nichols Vortrap, and of forming a paper in a sheet-mold according to TAPPI methods. This resulted in asbestos paper very low in magnetite. The mica paper was prepared by circulating scrap muscovite in a paper beater from which the dispersed mica flakes could be removed at the top and then formed into paper in a sheet mold by TAPPI methods. While these methods have made it possible to prepare both mica and asbestos papers from essentially domestic sources, there is still a need for higher temperatures in electrical insulating materials.

Mr. Callinan then reviewed briefly the progress on synthetic inorganic fibers as paper-making materials and indicated that, in addition to that made from fine glass fibers, paper has been prepared from both ceramic and silica fibers. All three of these fibers are now available commercially in sizes down to one micron or less in diameter. With this range of sizes available it is possible to use these fibers as water dispersed paper stock in standard paper-making machines without modification.

While the glass fibers and silica fibers are now commercially available, the ceramic fiber is still in an experimental stage of development. The glass fiber is free from slivers and slubs and can be used as required. The ceramic fiber which is prepared by rock-wool methods requires considerable treatment to remove shot and slubs. The silica fiber which is prepared by leaching fine glass fibers with acid is likewise free from shot and slubs and can be used after the acid, washing and drying treatment.

Mr. Callinan also described an interesting point which has arisen in the preparation of all three of these papers which, incidentally, have been produced in pilot plant runs at the National Bureau of Standards, in that all three types had high dielectric losses at elevated temperatures, apparently as a result of trapped ions. These three papers had been prepared with city water; however hand-prepared samples using silica and glass fibers but with distilled water showed no losses up to 150°C.

Mr. Van A. Wente in his talk described a new method which has been developed at the Naval Research Laboratory for making fine plastic fibers into sheets from commercially available silicone plastics. This new material, which is identified as "NaReL" combines the appearance of tissue thin paper with some of the draping qualities of cloth and yet uses neither paper-making nor textile-carding techniques. The basic plastics are heated and forced through fine slots, combined with air, and then sprayed onto a fine metal screen from which the resultant nonwoven fabric can be removed. Since this process requires neither critical paper-making nor textile machinery, the product should be less expensive material for possible longer-lived electrical insulation applications. Its dielectric strength is higher than glass and it will withstand an operating temperature of 250°F. The new material is also water repellent and may find potential application in protective clothing.

An interesting discussion period followed each paper.

The newly elected officers for the Section were installed at the close of this meeting.

* * *

At the previous meeting of the Section, which was held on March 20 at the National Bureau of Standards, the policy of hearing reports of the work of individual members was continued.

On this occasion, Sigmund Schuldiner of the Naval Research Laboratory described his investigations of determination of hydrogen overvoltage on smooth platinum. A portion of this work is the subject of a paper presented at the spring meeting of the Society in Philadelphia. The techniques and difficulties involved in such measurements were discussed, together with the description of a method for determining the surface cleanliness of the electrodes under study. The use of these methods made it possible to determine whether the surface of the electrode was contaminated by impurities. Also, by use of such techniques, very reproducible results were obtained on platinum in sulfuric acid. An interesting discussion period followed the talk.

Following the technical session, a short business meeting was held and the officers listed below were elected for the new term:

Chairman—R. S. Dean
Vice-Chairman—S. Eidensohn
Secretary-Treasurer—Fielding Ogburn

J. C. WHITE, *Secretary-Treasurer*

Alcoa's Texas Units Begin Production

The first of two new smelting lines at the Texas Point Comfort Works of the Aluminum Company of America recently started production. The new unit will bring Point Comfort's production capacity to about 135 million pounds of aluminum annually. The second line is scheduled for completion next month.

Electric power generated through the use of natural gas operates the new smelting facilities and, when their full production is reached, the gas consumption is expected to rise from the present 30 million cubic feet per day to about 50 million. The capacity of the power plant will be raised from 120,000 kw to about 200,000 kw.

Also under construction by Alcoa are two new aluminum smelting plants. One, at Rockdale, Texas, employs a lignite-burning steam power plant; the other, at Wenatchee, Washington, will use hydroelectric power.

American Potash Now a Sustaining Member

The Society is honored to add a new name to its list of Sustaining Members: the American Potash & Chemical Corporation, with headquarters in Los Angeles. The company is a major producer of primary chemicals, the principal products being potash, borax, boric acid, soda ash, salt cake, bromine, and lithium carbonate.

The company's plant is located at Trona, California, on the edge of Searles Lake in the Mohave Desert, 170 miles from Los Angeles. The chemicals are extracted from brine drawn from the lake. Since Trona operations began in 1916, the plant has produced almost 10,000,000 tons of chemicals for agriculture and for industry. The first potash manufactured in the United States was produced at Trona 36 years ago.

American Potash & Chemical Corporation employs 1700 at Trona, including subsidiaries, and a staff of 150 at its executive offices in Los Angeles and in its various sales offices. The principal officers of the corporation are Peter Colefax, President; W. J. Murphy, Vice-President in Charge of Sales; R. W. Mumford, Vice-President in Charge of Production; R. B. Coons, Vice-President in Charge of Industrial Relations; and D. S. Dinsmoor, Vice-President in Charge of Research and Development.

The corporation has five wholly-owned subsidiary companies: Borax & Chemicals Limited, of England, Trona Railway Company, Three Elephant Borax Corporation, Searles Domestic Water Company, and Searles Valley Development Company.

Indian Science Congress

The 39th Annual Session of the Indian Science Congress was held at Calcutta during the first week of January 1952. Papers read covered the various branches of science, and lectures, symposia, and discussions were held. There were a number of subjects of importance to electrochemists in which members of the India Section of the Society participated. The exhibition of scientific apparatus and instruments was of special interest.

Distinguished foreign scientists attended the session, including Dr. J. C. Warner, President, Carnegie Institute of Technology, Pittsburgh, and President of The Electrochemical Society.

T. L. R. C.

Symposium on Electroplating and Metal Finishing in India

A symposium on "Electroplating and Metal Finishing" was held at Jamshedpur on March 7 and 8, 1952, under the auspices of the National Metallurgical Laboratory. It was divided into two sessions on "Theoretical Aspects of Plating" and "Industrial Plating," covering electroplating, electropolishing, anodizing, and protective coatings. There was a good-sized gathering drawn from research laboratories, plating shops, industries, business firms, and government establishments. An exhibition of electroplated articles was also arranged.

The India Section of the Society was represented and papers were presented by members of the Section. T. L. R. C.

FRANCIS M. TURNER

Francis Mills Turner, 61, of Roslyn Heights, New York, and Atlantic, Maine, vice-president of Reinhold Publishing Corporation of New York City, died at Manhasset, New York, on April 3rd. He was a nationally prominent figure in the chemical world, as well as in technical book and magazine publishing circles.

Mr. Turner was instrumental in the founding or development of the Chemical Engineering Catalog, "Materials & Methods" magazine, the "Condensed Chemical Dictionary," and was the author or co-author of several books in this field.

Mr. Turner was an active member of The Electrochemical Society, which he joined in 1922, and had been committee chairman and member of several committees. He was the founder of the Turner Book Prize awarded annually to young authors in the Society.

PERSONALS

Solomon E. Barr is now chief chemical engineer and superintendent of metal finishing at the M & M Manufacturing Company, Trenton, N. J.

H. V. Udupa of S. Kanara District, Madras, India, is now at "Atira" P. O. No. 170, Ahmedabad, India.

Myron B. Towns has accepted the position of Head, Department of Chemistry, Tennesee A & I State University, Nashville, Tenn. Dr. Towns had been at Lincoln University, Lincoln University, Pa.

Emilio Jimeno Gil, Professor of Metallurgy at the University of Madrid, Madrid, Spain, was recently elected a full member of the Spanish Real Academia de Ciencias Exactas, Fisicas y Naturales. As is required of new members, Professor Jimeno gave a talk to a special reunion of this body in Madrid on April 2; his subject was "Science and Society."

Victor A. Hann, The Welsbach Corporation, Philadelphia, Pa., has been elected to the newly-created position of Executive Vice-President and to membership on the Board of Directors. Mr. Hann is one of the world's leading authorities on ozone generation.

Charles A. Thomas, president of Monsanto Chemical Company, St. Louis, Mo., was a recipient of the Missouri Honor Award for Distinguished Service in Engineering at the Engineer's Convocation at the University of Missouri on March 22.

William Pfanhauser, formerly president of Langbein-Pfanhauser Werke in Leipzig, has been living in Austria in recent years. His address is: Schloss Ehrenbichl, Bei Klagenfurt (Post Wolfnitz), Kaernsten, Austria. The Society has been informed that Dr. Pfanhauser, who is well known to many of our members, passed his 75th birthday on April 11; and good wishes are extended to him.

Victor Zentner has joined Surface Alloys Engineering Corp., Los Angeles, Calif., as a research chemist engaged in research and development in special plating processes and plating of alloys. Mr. Zentner left the Bureau of Standards, Washington, D. C., after completing a project there for the American Electroplaters' Society.

W. J. Kroll, consulting metallurgist, Corvallis, Ore., is scheduled to lecture at the International Powder Metallurgical Seminar which will take place in Reutte, Tyrol, on June 22–26.

Dodd S. Carr has joined the Bart Products Company, Inc., Belleville, N. J. Mr. Carr was formerly at the Research Laboratory of the International Nickel Company, Bayonne, N. J.

MEETINGS OF OTHER ORGANIZATIONS

INDUSTRIAL FINISHING EXPOSITION, annual meeting, International Amphitheatre, Chicago, Ill., June 16–19.

AMERICAN SOCIETY FOR TESTING MATERIALS, annual meeting, fiftieth anniversary, Hotels Statler and New Yorker, New York City, June 23–27.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS, summer general meeting, Hotel Nicollet, Minneapolis, Minn.

INSTRUMENT SOCIETY OF AMERICA, annual conference and exhibit, Cleveland, Ohio, September 8–12.

NEW MEMBERS

In April 1952, the following were elected to membership in The Electrochemical Society:

Active Members

HOWARD A. BEWICK, Solvay Process Div., Allied Chemical & Dye Corp., mailing add: 202 Newcastle Rd., Syracuse 4, N. Y. (Industrial Electrolytic)

JOHN H. BIGELOW, E. I. du Pont de Nemours & Co., mailing add: R.D. 6, Towanda, Pa. (Electronics)

JULES C. BOGEL, Schumacher's Radio Laboratory, mailing add: 1706 Church Ave., Brooklyn 27, N. Y. (Electrodeposition)

MIGUEL V. BOSCH, Cromado and Anodizado, mailing add: Reforma 714, Mexico 10, D.F. (Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

KENNETH J. BUSSE, Glass Fibers Inc., 1810 Madison Ave., Toledo 2, Ohio (Battery, Electric Insulation, Electrothermic, and Industrial Electrolytic)

GEORGE D. CREMER, Research Division, Solar Aircraft Company, San Diego, Calif. (Electrothermic)

RAY A. GRANACKI, Sarkes Tarzian Inc., mailing add: % Misiura, 1420 N. Washtenaw Ave., Chicago 22, Ill. (Screen Deposition)

ROBERT S. KARPIUK, Dow Chemical Company, mailing add: 613 Haley St., Midland, Mich. (Industrial Electrolytic and Theoretical Electrochemistry) Formerly Associate Member

WILLIAM E. KUHN, Titanium Alloy Mfg. Division, National Lead Company, Niagara Falls, N. Y. (Electrothermic)

WILLIAM H. LA HAYE, Acheson Graphite Plant, National Carbon Division, mailing add: Howard Apts., River Rd., Youngstown, N. Y. (Electrothermic)

LEWIS M. LEDERER, Inner-Tank Lining Corp., mailing add: 1097 Wade St., Cincinnati 14, Ohio

RICHARD W. LEWIS, Vidor Ltd., mailing add: 6 Bruce Rd., Downfield, Dundee, Angus, Scotland (Battery, Corrosion, Electrodeposition, and Industrial Electrolytic)

CHARLES H. LOWRY, Solvay Process Division, Allied Chemical & Dye Corp., mailing add: Box 271, Syracuse, N. Y. (Industrial Electrolytic)

ROBERT S. MACCORMACK, Columbia University, mailing add: 81 Morris Ave., Mountain Lakes, N. J. (Corrosion)

ROBERT T. MACDONALD, Superior Plating Inc., 1060 10th Ave., S.E., Minneapolis, Minn. (Electrodeposition)

ROBERT D. MILLER, Electric Auto-Lite, mailing add: 3721 Drakewood Dr., Cincinnati 9, Ohio (Electrodeposition)

JOHN F. ROSS, General Electric Company, mailing add: 3053 Warrington Rd., Shaker Heights 20, Ohio (Electronics)

RICHARD M. RULON, Sylvania Electric Products Inc., mailing add: 14 Beach Ave., Salem, Mass. (Electronics)

JOSEPH W. SAUSVILLE, Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio (Theoretical Electrochemistry)

JAMES C. SCHAEFER, Republic Steel Corp., mailing add: 5015 Montauk Ave., Parma 29, Ohio (Electrodeposition and Theoretical Electrochemistry)

FORBES S. SIBLEY, Dow Chemical Company, mailing add: 3209 Dartmouth Dr., Midland, Mich. (Industrial Electrolytic)

CHARLES N. WARD, National Carbon Company, mailing add: 4646 Terrace Dr., Niagara Falls, N. Y. (Electrothermic)

SAMUEL B. WYATT, U. S. Radium Corp., Whippany, N. J. (Electronics)

KEIICHI YOSHITOMI, Furukawa Battery Company, Ltd., 246, 2-Chome, Hoshikawa, Hodogaya-Ku, Yokohama, Japan (Battery)

Reinstatement

C. BRUCE BROWN, Dominion Tar & Chemical Company, Ltd., 2240 Sun Life Bldg., Montreal, Quebec, Canada (Industrial Electrolytic)

Associate Member

ABRAHAM L. LEVINE, The Electric Storage Battery Company, mailing add: 7531 Overbrook Ave., Philadelphia 31, Pa. (Battery, Corrosion and Electrodeposition)

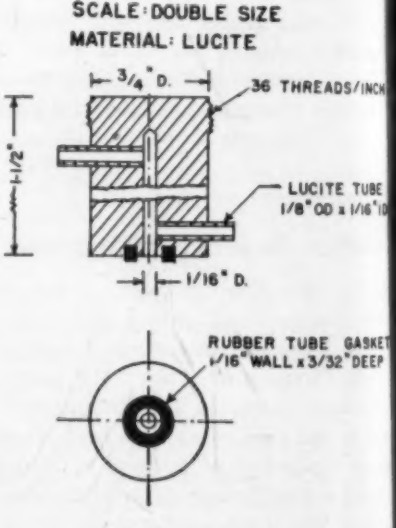
Student Associate Member

CHARLES E. SCOTT, University of Cincinnati, mailing add: 8344 Curzon Ave., Cincinnati 16, Ohio (Electrodeposition)

LETTER TO THE EDITOR

A Micro-Cell for the Film-Indent Potential Measuring Technique

Smith and Pingel (*J. Electrochem Soc.* **98**, 48, 1951) describe in their article a procedure wherein a metal, mounted in Lucite and polished and etched, is covered with a transparent film of plastic material. This film is then pierced at any desired location on the metal surface with an indenter, using a microhardness tester. The solution potential of the small area of the metal exposed by the indentation is then determined by immersing the sample in an electrolyte, using a calomel half-cell and a suitable potentiometer.



MICRO-CELL

In applying this film-indent technique to a study of the mechanism of stress corrosion, the author has devised a so-called micro-cell. This micro-cell, fabricated to fit the base of a standard objective lens, is mounted on a three-position revolving nosepiece of a metallurgical microscope. By virtue of its

cation on the nosepiece along with an objective and an Erb-Gray Microhardness tester, the micro-cell is centered directly over the indentation which had been made at a chosen location (grain boundary or grain center). The cell is lowered into position and the electrolyte is introduced into the upper arm of the cell from a flask which is used as a junction between the salt bridge and the calomel half-cell. The lower arm of the cell is closed with a clamp after allowing the electrolyte to flow momentarily.

The construction of the cell is quite simple, being made of 1-in. diameter pyrite rod (Fig. 1). The most important part of the cell is the gasket. It has been found necessary to grind the rubber tubing after positioning it in the cell to insure a leak-proof seal when the cell is in place.

The advantages of this cell are quite numerous in that the metal sample, once pierced, need not be removed from the microscope for potential measurements; handling of the various components of the film-indent technique is reduced to a minimum; the indentation can be easily checked after the potential measurements have been made; and, potential measurements can be made at points that are relatively close with great accuracy as to location. As indicated this micro-cell is being used to measure potentials in a sample as stress is applied to the sample. A report on this technique will be forthcoming in the future.

L. W. Gleekman
University of Delaware,
Newark, Delaware

BOOK REVIEWS

Industrial Heat Transfer by F. W. Hutchinson. Published by The Industrial Press, New York, 1952. 326 pages, $6.00.

Professor Hutchinson has prepared a compendium of curves for the rapid approximate solution of 128 heat transfer design calculations and problems. The graphs include 5 on mean area and conduction through tube walls, 11 on radiation factors, including human beings, 8 on calculating Reynolds, Prandtl, Grashoff, and Nusselt numbers from their defining quantities and vice versa, 12 on film coefficients for streamline flow and similar conditions, 5 for multiplying the local coefficient by the inner or outer area per lineal foot of a number of commercial tube sizes, and 9 on miscellaneous overall coefficients, etc., from the film coefficients. Turbulent flow normal to a pipe and heating and cooling inside of a pipe are represented by 43 graphs for commercial chemicals and 38 for gases and vapors. The page opposite each graph lists the equation or equations on which the graph is based, limitations, and a sample calculation. The last 81 graphs mentioned above have the physical properties "built into" them and are all based on the equations $Nu = 0.023\ (Re)^{0.8}\ (Pr)^{n}$ inside of a pipe, where $n = 0.4$ for heating of liquids and 0.3 for other cases, and $Nu = 0.385\ (Re)^{0.56}\ (Pr)^{0.3}$ normal to a pipe. In addition there are some 52 pages on elements of heat transfer theory, particularly the equations used in the graphs, and 6 compact pages of dimensions and properties of tubes.

On the debit side might be cited that the graphs have no fine subdivisions, and that the diagonal "transfer lines," which are used to avoid vertical scales, cause extra steps and decreased accuracy. Also, on the condensation and boiling graphs, the film coefficient might have been replaced, to avoid the trial-and-error required in most problems. It might also be pointed out that about half of the page opposite each of the last 81 graphs is used up in repeated restatement of the equations, references, etc.

On the credit side, may be listed the attractive appearance and durable construction, and the undoubted saving in time that is possible through the use of the curves, particularly the last 81. This book does not seem generally suitable for use as a text in Heat Transfer courses, but it should prove a boon, in particular, to plant engineers, and also to those design engineers who may prefer a quick approximate answer to the usual more laborious procedure.

C. F. Bonilla

Analysis of Electroplating and Related Solutions by K. E. Langford. Published by Electroplating and Metal Finishing, Teddington, England, 1951. xi plus 387 pages, $8.00.

The book will undoubtedly be welcomed throughout the English speaking world, since it answers a long-felt need for a compilation of well-established methods of analysis of plating solutions. The author knows what has been needed and has succeeded in his task of presenting in clear concise form the best and most reliable methods of analysis. Considerable thought has gone into producing a reference text that is practical as well as informative. As far as the reviewer can see all of the important solutions used by electroplaters in this country have been dealt with. Over 300 methods for the determination of principal constituents and impurities in electroplating solutions are given, together with chapters on Sampling, the Control of Cleaners, Pickles, Dips, Etches, Phosphating Solutions, Electrobrighteners, the Analysis of Plating Salts and of Water, Physical and Physico-Chemical Methods of Analysis, the Preparation of Standard Solutions for Volumetric Analysis, and a good selection of Tables.

The reviewer wonders if a line or sentence has been omitted at the bottom of the first paragraph of page 25 where the solution is made alkaline instead of acid just before the titration with ferrocyanide. Two further minor objections are, first, that the cost of the book seems high considering the rather mediocre binding and, second, from the standpoint of the American plater or chemist, the calculations to oz/gal will be of little value since they are based upon the Imperial gallon.

C. L. Luke

RECENT PATENTS

Selected for electrochemists by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

January 29, 1952

Schloen, J. H., and Franchetto, L. V., 2,583,799, Electrolytic Process of Preparing Selenic Acid from Selenious Acid

Smith, L. H., 2,583,898, Vapor Phase Electrochemical Process

Smith, L. H., 2,583,899, Electrochemical Process

February 5, 1952

Elrod, H. G., J., 2,584,117, Circulation of Cell Electrolyte

Aller, C. B., 2,584,317, Method of Producing Bimetallic Printing Forms

Sonnino, C., 2,584,400, Process for Anodic Oxidation of Aluminum and its Alloys

Ferrand, L., 2,584,565, Fused Bath Electrolytic Cell for the Production and Refining of Metals

Richards, W. F., 2,584,615, Thermocouple Device

Richards, W. F., 2,584,616, Thermocouple Device

Schneider, W. R., 2,584,623, System

and Method for Protecting Pipes and Other Current Conducting Structures Against Electrolytic Corrosion

Alden, C. R., 2,584,654, Heater for Moving Electrolytes

Sands, M. L., 2,584,816, Electroplating Control System

Vanharen, L., Rossier, M., and Vandeur, L., 2,584,824, Electrolytic Preparation of Alkali Metal Chlorites

Viarengo, J. P., 2,584,946, Battery Lid

February 12, 1952

Godshalk, J. B., and Medlar, L. A., 2,585,005, Method and Apparatus for Charging Batteries

Juvrud, M. O., 2,585,014, High-Voltage Rectifier Disk

Wallace, C. F., 2,585,059, Electrical Cell Apparatus for Detecting Chemical Characteristics of Liquids

Wallace, C. F., 2,585,060, Electrical Cell Apparatus for Testing Liquids

Hirsch, B. L., 2,585,461, Method of Making Fluorescent Zinc Oxide

Bull, C. S., and Atherton, A. H., 2,585,534, Secondary Electron Emissive Electrode and Its Method of Making

Lübeck, C. H. O., 2,585,564, Closure for Tanks Containing Battery Cells

Strickman, S. W., 2,585,700, Method of Making Conductive Designs

Dorst, S. O., 2,585,752, Production of Discontinuous, Conducting Coatings Upon Insulating Surfaces

Gallois, R., 2,585,761, Electric Glass Melting Process

Klein, S., 2,585, 791, High-Temperature Electric Resistance Oven

Marks, H. C., 2,585,811, Electrochemical Method of Automatically Determining Available Chlorine in an Aqueous Liquid

February 19, 1952

Gray, A. G., 2,585,902, Inhibition of Oxidation in Tin Solutions

Ellis, G. B., 2,585,922, Hermetically Sealed Alkaline Dry Cell

Lilienfeld, J. E., 2,585,947, Electrolytic Condenser for Alternating Current Power Circuits and Method of Operating the Same

Coltman, J. W., and Longini, R. L., 2,586,304, Protection of Phosphors from Attack by Alkali Vapors

Grusell, A. E., Sandmark, H. O. A., and Hysing, E. G., 2,586,426, Galvanic Primary Cell

Harty, E. A., 2,586,539, Metal Rectifier Assembly

Bahney, L. W., 2,586,596, Induction Pouring Furnace

Hart, J. L., 2,586,649, Recovery of Indium Values as Indium Arsenate

February 26, 1952

Seaborg, G. T., and Gofman, J. W., Application 25,076, Electrodeposition of a Heavy Metal-Containing Material

Bash, F. E., 2,586,768, Vacuum Tube Electrode Element

Liebson, S. H., 2,586,836, Iodine Counter

LITERATURE FROM INDUSTRY

COLLOIDAL GRAPHITE. New four-page brochure contains photographs, diagrams, charts, and information on the advantages of colloidal graphite over ordinary petroleum lubricants in the assembly and run-in of machines. Acheson Colloids Company, Division of the Acheson Industries, Inc. P-36

BORIC ACID POWER FUSES. Illustrated booklet entitled "Boric Acid Power Fuses" describes the complete line of power fuses for compact and economical short-circuit protection. Discusses 3 types of fuses with ratings, construction, operating characteristics, and applications for each type. Westinghouse Electric Corporation. P-37

BETTER ANALYSIS. New issue of Better Analysis, a periodic review of the theory and practice of instrumentation, is released. Emission spectroscopy with several interesting applications is described. Baird Associates, Inc. P-38

PRACTICAL NICKEL PLATING. A 44-page general publication with over 40 illustrations, tables, and charts. Provides the designer, specifying engineer, and user with basic information on electroplating and detailed information on nickel plating and its practices. Recommendations on preparation of basic metals, recognition and correction of plating difficulties, etc. International Nickel Co., Inc. P-39

NEW PRODUCTS. New Product Bulletin on 3-Aminopropanol gives technical data and various potential applications, as corrosion inhibitor, etc. American Cyanamid Co. P-40

CONTROL SELECTION BULLETIN. Eight-page selection guide for a wide range of electric and electronic controls, devices, and accessories is now available. General Electric Co. P-4

TEST INSTRUMENTS. A condensed four-page catalogue and price list which contains illustrations of all the Simpson Test Instruments and Panel Meters, including the new Model 276 Oscilloscope Calibrator, is available. Simpson Electric Company. P-4

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

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CONFIDENTIAL PROJECT in organic electrochemistry. Requires Ph.D. or equivalent industrial experience to head original research requiring exceptional talent, independent thinker, strong theoretical background. Reduction to commercial process will proceed concurrently with theoretical phase following which position open for permanent connection supervising this development. $5000–$7500. Location Detroit. *Reply to Box A-239.*

Position Wanted

ELECTROCHEMIST, M.S., 7 years' research and development experience in primary and storage batteries; also excellent theoretical background in electro-organics and electrometallurgy. Desires position in the New York metropolitan area. *Reply to Box 348.*

Editorial

The Electric Insulation Division

THE ELECTRIC Insulation Division was founded to promote the attainment and dissemination of knowledge pertaining to dielectrics. This subject is a division of science dealing with the electrical, mechanical, and chemical properties of nonconductors of electricity. It is composed of four branches of specialized study under the titles, Theoretical Dielectrics, Materials, Instrumentation and Measurements, and Applied Dielectrics or Electric Insulation. The use of synecdoche by the founders of the division shows their practical thinking and their bent toward the application of knowledge.

The first named branch of dielectrics deals with polarization, Maxwellian losses, Faraday currents, Dipole Moments, dielectric rupture, conductivity, chemical reactivity, thermodynamics, and quantum phenomena. Entire volumes have been written on each of these subdivisions of theoretical dielectrics; for example Debye, Smythe, and Le Fevre have each published works on Dipole Moments alone. "Materials," studied as dielectrics, include all gases, liquids, and solids which do not conduct electricity at constant potential and low gradients. Hence the study of the mechanical, chemical, and electrical properties of paper, plastics, synthetic and natural oils, ceramic and natural insulators such as mica and asbestos are included as subjects for study within this branch of knowledge. Since the relative conductivity of each of these items is a function of the purity and processing involved in their manufacture, preparative methods are considered parts of Materials Dielectrics. The methods by which these conductivities, dielectric constants, dielectric loss factors, dielectric strengths, and arc resistances of insulators are determined, are constituents of that part of knowledge considered as Dielectric Measurements. Finally the systematic knowledge of practical dielectrics, including the manufacture, employment, and efficiencies of such items as condensers and capacitors, wires and cables, terminals, bushings and panel mountings is considered under the title of Applied Dielectrics.

Six papers have been prepared for this commemorative issue each presenting a facet of knowledge of the foregoing interests of the Division under the title, "Fifty Years of Electric Insulation."

—THOMAS D. CALLINAN

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Fiftieth Anniversary

FIFTY YEARS OF ELECTRIC INSULATION

General Introduction

Thomas D. Callinan*

The economic transmission of power was the primary problem in electrical engineering during the first half of the present century. The solutions are classic; they include the development of power transformers, the fabrication of impregnated cables, and the successful production of insulated wire. These items solved the problem of moving large packets of hydroelectric power at high voltages, underground, through populated areas to distribution stations where the energy could be utilized with compact equipment. In the development of these items, the electrical engineer contributed the theory of laminates and the chemist the thermally stable gases, liquids, and solids essential to the reduction of electrical units from drafting boards to articles of commerce.

There was neither orderliness nor direction in the solution of the problem, but ultimately resolution occurred in the two concepts of dielectric strength and life-expectancy. One led to the requirement of engineering continuity and the other to the requirement of chemical stability. On the one hand, the theory and practice of impregnated laminated structures was developed into the engineering science of today. It resulted in the attainment of dielectric strengths in excess of 3 Mv/cm. On the other hand, the utilization of the ten-degree law of chemistry led to the synthesis and commercial availability as dielectrics of the nonflammable, thermally stable, chemically inert organic materials of today. The scientific pioneers developed the resins as substitutes for shellac, the chlorinated materials as substitutes for the flammable mineral oils, and the tissues as substitutes for the wrapping papers and tapes. The electrical industry has stimulated developments in the field of materials which have long ago forgotten their first customer. The answers to the various engineering problems of that period appeared in almost exact five-year steps, i.e., bakelites, kraft tissues, alkyds, chlorinated benzenoids, glass yarn, silicones, fluorinated polymers, and lately the inorganic papers.

* Naval Research Laboratory, Washington, D. C.

Lagging the primary problems by a quarter of a century and now in its zenith of effort is the problem of the reliable transmission of intelligence. It differs markedly from the first problem though it is often confused with it. The factors involved relate to the engineering aspects of capacitance and operational stability.

Great success has been met in the power range of the frequency spectrum. The geometry of the armature-type capacitor was reduced by the development of 25 micron tissues and films. The apparent dielectric constant was increased by the development of the polar molecules. The reliability was improved by the substitution of chemically inert bodies.

In the shorter wavelengths, the campaign is fluid; the engineer finds himself increasingly dependent on materials of the presynthetic era—on mica, steatite, and ceramics.

The chemist skilled in the lore of the carbon derivatives finds himself in the terra incognita of adjacent areas of Mendeleeff's chart. Again he finds himself handicapped increasingly by logistic and combat efficiency problems. The reliable transmission of intelligence is increasingly dependent on resistance to mechanical, radiational, and thermal shock. Studies have been made on the efficiency of items currently available, but generally the lists degenerate to catalogues of progressively less useful products.

Although eighty per cent of the half-century related to the solution of the problem of the economic transmission of power, some of the secondarily important problems of that era are with us today including necessity for improved moisture resistance, higher impulse breakdown levels, and greater stability in the presence of metals. The vitalizing force, however, at the beginning of this fifty-year period is that of the shock spectrum. Already a host of inorganic papers and gases of both natural and synthetic origin have appeared. The titanates and the transistor have also made their bows. The development of the inorganic fluids and varnishes is awaited earnestly.

Dielectric Breakdown in Solid Insulation

*J. J. Chapman**

A number of very valuable review articles devoted partly or wholly to the present subject have appeared during the past few years. These serve a useful purpose in depicting our progress, as well as providing extensive bibliographies of lasting value. The review by Burnham (1) shows the extensive use of pure science being applied to the study of dielectric breakdown. A comprehensive report by Javitz (2) demonstrates that practical consideration must govern many investigations today. A later report by the same author (3) predicts the use of many new materials of exceptional dielectric strength. The survey by Kline (4) illustrates the diverse fields of investigation motivated toward the goal of better materials. Clark (5), in a recent publication, discusses some of the outstanding achievements of industrial research and thereby illustrates the close connection between chemistry and electricity. Von Hippel (6) reminds us that research from the standpoint of basic science is quite often the harbinger of the spectacular and unpredictable developments of industry.

Trend of Investigations

The Wagner (7) theory of thermal breakdown for many years entered prominently into discussions of the dielectric breakdown of solid insulation. As many new materials and conditions of usage occupied the attention of engineers, a variance of opinion was inevitable. Additional results and interesting discussion are given by Wagner (8) in which the breakdown of materials is examined with respect to frequency and temperature.

Von Hippel (9) started a new approach to the problem of solid dielectric breakdown that has engaged workers in theoretical and experimental activities for more than a decade.

Keller (10) presents interesting new data on glass, using surge voltage techniques, and obtained curves somewhat reminiscent of Montsinger's volt time variation (11) for oil-impregnated pressboard. In Keller's work, however, the flat region is barely suggested by the data; this was an interesting feature of Montsinger's curve between 10^{-5} and 10^{-1} seconds. Keller discusses his results in the light of theoretical conceptions from the Frohlich school of thought (12, 13).

In this paper and others that follow in this review, the magnitude of conduction currents prior to breakdown occupies the attention of investigators. In this connection the careful technique of Race (14) is of continued interest.

Oakes (15) presents results of direct current breakdown tests on polythene, polystyrene, polyisobutene, and polymethylmethacrylate over a range of temperatures, −200° to 110°C. He also introduced chlorine and oxygen into respective groups of polyethylene samples so as to form scattering centers and thus conduct tests of Frohlich's conception of a critical temperature.

Bird and Pelzer (16) examined polyethylene with particular regard for crystallite formation and conclude that this effect causes no significant change in the direct current breakdown strength.

Ball (17) studied the direct current electric strength of polyvinyl alcohol from −195° to 80°C and compares his results with other workers. In the discussion involving Frohlich's theory a general area of agreement is outlined, but uncertainty as to the critical temperature persists.

Polyethylene and polystyrene have been regarded by many electrical engineers as very nearly perfect dielectrics unblemished by structural defects or time-dependent polarizations. Possibly closer scrutiny will indicate that these compounds can yet attain an even higher degree of excellence. Matheson and Caldecourt (18) have studied time-dependent displaced charge in polystyrene. It is not unlikely that such displaceable charge may affect the breakdown strength of this material.

In a paper of historic importance because it presaged the future importance of the Conference on Electrical Insulation of the National Research Council, Whitehead (19) proposed that fundamental properties might well be studied further in the direct current case before entering the anomalies to be encountered in alternating current investigations. It is noteworthy that this opinion has been widely shared, for that much of the search for the ultimate nature of dielectric breakdown has been through the use of direct current voltages.

Industrial and military applications have necessarily carried us forward with great impatience into development using high frequency and extremely rapid pulse voltages. The demand for design data far outweighs the growth of established theory and laboratory data.

Hurd (20) in a review paper makes note that symmetrical molecules have been observed to exhibit higher impulse breakdown strength than unsymmetrical molecules of similar chemical composition. The observations were made with a breakdown electrode of sharp contour.

The author with coworkers (21) has found that many materials show a considerable decrease in dielectric strength in going from 60 cycles to 18 megacycles (recently extended to 101.9 megacycles). Like dielectric constant, but without exception, the breakdown strength of solid insulations shows important decrease with increasing frequency.

Summary

The predominant view appears to be that dielectric breakdown is electronic in nature, although other mechanisms may influence the final physical appearance of the puncture and indeed affect the magnitude of the voltage required for rupture.

Efforts to prove the electronic nature of failure have given hope for a theory similar to the Townsend avalanche for gases, with modifications stemming from the ideas of Von Hippel and Frohlich. A concise explanation of criteria for breakdown comparing these two schools of thought was given by Murphy (22) in covering a wide range of literature that continues to be of interest.

However, complete verification without stint of doubt has not been obtained for either modification of the Townsend theory as applied to solids. Proper test of such ideas requires ideal materials, which are not available to all desired specifications; hence, other effects of a compromising nature enter the experiments. Materials that are of advantage in practice are sufficiently different from those of controlled experiments as to raise serious questions in the application of theory.

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It has been established, however, that the direct current dielectric strength in low temperature regions is comparatively high for many solids. A region of decreasing strength with the generally expected "knee shape" is found upon increasing temperature. This would correspond to an increase in conduction bands as predicted by Frohlich for a critical temperature. However, the behavior of the breakdown curve approaching this region is not always as expected, and considerable doubt as to the location of the critical region ensues.

Exploration at higher frequencies may reveal that molecules with scattering centers present a changed target for accelerated electrons, as compared to the direct current case. Also, lack of certain slow polarizations because of their time dependence may change the character of the brief liason between accelerated electrons and the component structures of the dielectric.

REFERENCES

1. J. Burnham, "Digest of the Literature of Dielectrics," XIV (1950), NRC Conference on Electrical Insulation.
2. A. E. Javitz, *Elec. Mfg.*, **47**, February, 101 (1951).
3. A. E. Javitz, *Elec. Mfg.*, **49**, January, 90 (1952).
4. G. M. Kline, *Modern Plastics*, **29**, 5 (1952).
5. F. M. Clark, *Gen. Elec. Rev.*, **54**, 11 (1951).
6. A. Von Hippel, *Electronics*, **24**, 126 (1951).
7. K. W. Wagner, *Arch. Elektrotech.*, II **9**, 371 (1914).
8. K. W. Wagner, *Arch. Elektrotech.*, **39**, 215 (1949).
9. A. Von Hippel, *J. Applied Phys.*, **8**, 815 (1937).
10. K. J. Keller, *Physics*, **17**, 511 (1951).
11. V. M. Montsinger, *Elec. Eng.*, **54**, 1300 (1935).
12. H. Frohlich, *Nature*, **151**, 339 (1943).
13. H. Frohlich and J. H. Simpson, "Advances in Electronics, II," Academic Press Inc., New York, 1950.
14. H. H. Race, *Gen. Elec. Rev.*, **44**, 445 (1941).
15. W. G. Oakes, "Proceedings of the Institution of Electrical Engineers," **96**, Part 1, 37 (1949).
16. D. W. Bird and H. Pelzer, "Proceedings of the Institution of Electrical Engineers," **96**, Part 1, 44 (1949).
17. L. D. Ball, "Proceedings of the Institution of Electrical Engineers," **98**, Part 1, 84 (1951).
18. L. A. Matheson and V. J. Caldecourt, *J. Applied Phys.*, **22**, 1176 (1951).
19. J. B. Whitehead, *J. Am. Inst. Elec. Engrs.*, **42**, 1297 (1923).
20. D. T. Hurd, *Gen. Elec. Rev.*, **51**, December, 26 (1948).
21. J. J. Chapman, J. W. Dzimianski, C. F. Miller, and R. K. Witt, *Elec. Mfg.*, **48**, July, 107 (1951).
22. E. J. Murphy, "Digest of Literature on Dielectrics," XII (1948), NRC Conference on Electrical Insulation.

Electric Insulation Developments: Cables

*J. A. Szilard**

The main objective in the development of insulated wires and cables during the first half of this century was to make them better both electrically and mechanically and at the same time reduce costs. It is safe to prophesy that this will remain the objective of the cable makers for the second half of this century.

The present multiplicity of insulated wires and cables started with about six main types in use at the turn of the century. These were: paper power cables, rubber cables, varnished cambric cables, weatherproof wires, magnet wires, and paper telephone cables. This review is based on the most important advances which occurred in the design of these six basic types.

At the start of the century there was a rivalry between paper and rubber cables for the high tension field, at that time up to 25 kv. This competition was decided in favor of oil-impregnated paper cable and today, for the highest voltages and for large blocks of power, this cable type is generally used. In fact, this is the only type of cable insulation available at present which is suitable for use above about 35 kv. It is in actual operation up to 230 kv and is potentially available for still higher voltages. Originally the paper used was made of manila rope and the impregnating compound consisted of various combinations of rosin oil, rosin, castor oil, later of petrolatum and of other mineral oils. Today the paper is made of wood pulp and the compound is either a naphthenic base mineral oil or synthetic polybutene base oil. The oldest and most widely used paper power cable is the "solid type" in which no special provision is made to compensate for the expansion and contraction of the oil-impregnated paper insulation during load cycles; for this type an extruded lead sheath is used as the outer covering. Solid type paper power cables are used for transmission and distribution largely by the electric utilities at voltages as high as 69 kv although at the present time the usual upper limit is 35 kv. For very high voltages, 138 kv and higher, the oil filled type was introduced around 1930. In this design the impregnating oil is of low viscosity. The line is equipped with oil reservoirs at intervals and the oil flows longitudinally in channels provided in the cable into these reservoirs with the expansion of the insulation due to heat, or is forced from the reservoirs back into the cable when the insulation cools. An alternate is the pipe type cable in which a steel pipe, protected on the outside against corrosion, is buried in the ground. Oil-impregnated paper insulated conductors are drawn into the pipe and the pipe is filled with oil or gas operating under pressures of the order of 200 psi. Pressure of this order eliminates the possibility of ionization within the insulation of the cable. Low pressure gas filled cables using nitrogen up to 15 lb pressure are operated with marginal ionization within the insulation. These cables are in a lead sheath and the gas pressure is utilized as a signal system in case a leak develops in the lead cover. About the time of the 1920's, grounded shielding of the individually insulated conductors of multiconductor cable was introduced. Today shielded cable is the generally accepted type for moderate and high voltages. The normal maximum operating temperature for paper power cables varies with operating voltage from 70° to 85°C and the emergency maximum from 90° to 115°C.

While paper power cable proved to be the more suitable in the high tension field, rubber cable became the most widely used type in the low voltage field because of its elasticity, flexibility, moisture resistance, and ease of splicing. At the turn of the century wild South American para rubber was the basic raw material with sulfur as the vulcanizing agent and inorganic fillers making up the rubber compound. After World War I, plantation rubber grown in the

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Far East became more and more widely used in rubber cables. After 1920, the use of accelerators to speed the vulcanizing process and antioxidants to prolong the life of rubber insulations became quite general. Other developments in the 1920's were the use of purified rubber for compounds with low moisture absorption, the development of latex insulated wires, and the use of heat-resistant rubber compounds. At about the same time, ozone-resistant rubber compounds, the so-called oil base compound, which contain vulcanized oils and bitumens and which have been in limited use since the start of the century, were further developed and became generally used. The 1920's and 1930's have seen the development of rubber insulated wire constructions for special uses such as the flame-resistant building wires, nonmetallic sheathed cables for house wiring, flexible cords, service entrance cables, which eliminated the conduits from the side of buildings, x-ray cables, small ignition wires, etc. This incomplete list is an indication of the great multiplicity of rubber insulated cables.

The first synthetic rubbers used commercially on wires and cables in the early 1930's were the polysulfide rubbers (thiokol) and the polychloroprene rubber (neoprene). Both are comparatively poor as insulation but excellent as protective jacket materials because of their oil, solvent, and acid resistance. The first serious challenge to the hegemony of the rubber cables in the low voltage field came from the plastic cable in 1938, utilizing plasticized vinyl resins. Until about 1938 all building wire was made with rubber insulation and cotton braid, impregnated with flame-retardant bituminous compounds and a final coat of colored lacquer for circuit identification. In contrast, with the use of vinyl resins, it was possible to design a building wire which consisted of a single extruded layer of plastic insulation, in any color, with tough abrasion-resistant and flame-resistant covering. At the start of World War II, plastic insulated building wires were already in use and during the war the vinyl plastics were utilized extensively for shipboard cables both as insulation and jacket material. The synthetic rubbers and plastics really came of age in World War II. Some of the synthetic rubbers are useful both as insulations and as jackets; others can only be used for protective jackets. GR-S replaced natural rubber during World War II in wires and cables. This replacement became permanent in most applications. The special GR-S type manufactured to the specification of the wire and cable industry proved a very satisfactory rubber for insulation and also for jacket compounds. GR-S has better heat, oxidation, and weather resistance than natural rubber. Butyl rubber (GR-I), developed originally for automobile tire tubes, has been used in recent years to some extent for the insulation and protective jackets of cables. This material has good heat, ozone, and moisture resistance. Buna N cannot be used for insulation but has been used for oil-resistant jackets, and has also been proposed as a plasticizer for vinyl jackets. Silicone rubbers have been developed since 1945 for use at service temperatures up to 200°C. Their cost is still high and their physical properties are still inferior to ordinary rubber compounds.

In the plastic field, next to vinyls, polyethylene has perhaps the most interesting record so far. Polyethylene insulated cables have been in use since 1944, at first mostly for high frequency applications. The splendid electrical properties and excellent moisture resistance of polyethylene are somewhat offset by its low melting point and poor resistance to point discharge where local overheating may occur. It has not been used as yet to any great extent in power cable For tough abrasion-resistant jackets on communication cable over polyethylene insulation, polyamides (nylon) have be used. Polystyrene, in the form of disks or spirals, has be used as spacer material for high frequency coaxial cable Some insulated wires and cables have already been fabricate with the fluorocarbons, particularly with polytetrafluor ethylene (Teflon) and polymonochlor trifluoroethylene (Kel-F and Fluorothene). These fluorocarbons are comparable t polyethylene in electrical properties; they are, in addition inert to all chemicals, have high softening points, and ar flame-resistant, but have low corona resistance. The hig price of these fluorocarbons combined with processing pro lems have prevented any widespread use of these materia to date in the cable field.

Rubber or plastic insulated cables are now in general us for power transmission up to 15 kv and in limited applica tions at higher voltages. Indeed, even in the early 20t century such cable was installed for use at 25 kv. During th past decade, the use of shielding with conducting or semi conducting layers both over the conductors and over th insulation became generally accepted. The temperature rang for rubber cables is up to 80°C, for silicone rubbers up t 200°C, for vinyl plastic insulated cables up to 85°C, fo specially compounded vinyls up to 105°C, and for the fluoro carbon cables up to 200°–250°C.

Paper power cables and rubber cables are of dominating importance in the cable industry. Thus, the changes in these overshadow changes in other types. Nevertheless, the changes in other cable types have also been noteworthy.

Varnished cambric cables were first made in 1902. The varnished cloth is made by coating closely woven cotton fabric on both sides with a good grade of varnish. The properties of this type of cable represent somewhat of a compromise between the properties of paper and rubber cables. Like paper power cables, varnished cambric cables have high dielectric strength and good ozone resistance, but unlike paper cables they may be used without lead sheath where installation is in relatively dry locations. Varnished cambric cables are also easier to install than paper cables. The flexibility of this cable depends on the free sliding of the layers of varnished cambric tapes. The trouble due to the sticking of the layers was overcome by improved varnish materials around 1912. Since then the quality of the varnished cloth has been continuously improved. These cables too have been used extensively for shipboard cables during World War II. The temperature limit for varnished cambric cable is 85°C. Silicone and even fluorocarbon-coated glass tapes are now available but have not been used except on experimental cable construction. The cost of these tapes is rather high.

Weatherproof wires for overhead distribution have been made for many years with asphalt-impregnated textile coverings over the conductor. In 1932 the URC type (Utilities Research Commission) was developed. The main feature of this type was the improved weather resistant asphalts used in and over the textile coverings. After World War II, wires with extruded neoprene or polyethylene coverings, instead of the textile-asphalt coverings, were introduced.

In paper telephone cables, the most spectacular of fairly recent development has been the attempt to replace lead which is both expensive and in short supply, with another sheath material. A corrugated aluminum tape sealed with a polybutene base cement and covered with extruded polyethylene has now been in use for several years as a jacket over paper insulated telephone cables. There were some initial

difficulties with the new jacket due to environmental cracking of the polyethylene. These have now been corrected. However, this combination jacket has not been in use long enough to permit a final evaluation. Other changes on telephone cables have been primarily in the use of smaller conductors and in the increase of number of pairs in the cable all of which were brought about by equipment development.

Magnet wire up to 1900 was insulated only with cotton, paper, or silk. The big change came about 1900 when enamel wire was first made by applying a varnish in the form of a thin film to copper wire. Enamel wire, due to its excellent space factor and good electrical properties, became used more and more until, with the development of the radio industry around the middle 20's, enamel wire production increased tremendously. The next forward step came in the middle 30's when synthetic wire enamels, particularly vinyl acetalphenolic resin base, also polyamid base, were developed to improve on the abrasion, and heat- and solvent-resistance of the original conventional oleoresinous enamel wire. It is of interest to note here that these developments were primarily to facilitate fabrication (coil winding and varnish treatment) rather than to improve the electrical properties of the enamel film. In recent years polyester base enamels joined the available synthetic wire enamels. High-heat-resistant enamel wire is now made on a limited scale with fluorocarbon (Teflon) dispersion with and without an inorganic undercoat.

In addition to the cotton and silk, asbestos and paper insulated magnet wires have been manufactured since the 1920's. Paper magnet wires with bare copper or enamel wire base have excellent space factor and good abrasion resistance. Glass yarn insulated magnet wire with varnish impregnation has been made since 1936 and for higher temperatures silicone varnish impregnated glass magnet wire has been available since 1946.

Asbestos fixture and stove wires with carded asbestos fibers or wrapped asbestos roving, both types impregnated with flame- and moisture-resistant compounds, have been manufactured since about 1930. Braided asbestos cables have been used in dry locations at temperatures up to 200°C. More recently all mineral insulated wires and cables have been introduced for continuous service up to 250°C. This cable has a magnesia insulation and a copper or other metallic sheath. The magnesium oxide insulation being completely inert cannot be ignited, sustain combustion, or convey fire from one location to another.

This review of the improvements of electrical cables by the use of new materials and changes in design indicates that steady progress has been made since 1900 in the direction of increasing the expected life of cables and at the same time improving their operating efficiency. Increased resistance to heat has been one of the primary objectives because it provides the basis for obtaining improvement of both of these factors by decreasing the rate of chemical deterioration and also permitting heavier load conditions. The ideal all-purpose cable insulation is not yet available. It probably will be necessary, for many years to come, to use a variety of materials to obtain the variety of characteristics for the many service conditions under which cables are expected to operate

Electric Insulation Developments: Plastic Compounds

*Leon L. Deer**

Three classes of insulation materials have been available to the electrical industry since its beginning: an inorganic group composed of slate, mica, glass, and ceramics; an organic group consisting of amber, waxes, tars, raw rubber, and pitches; and a modified organic group of animal or vegetable fibers, wood, and paper.

Materials in the first class are extremely hard to fabricate into intricate shapes, and they are also quite brittle; however, they have the ability to withstand high temperatures. The other two groups, organic by nature, have the following disadvantages: flammability, limited resistance to heat, brittleness, low tensile strength, inflexibility, high water absorption, and rather poor electrical properties.

The electrical industry, with its increasing demand for easily fabricated materials which have outstanding electrical properties, called in the research chemist. His answer to the problems was modification of the natural products, and manufacture of synthetic organic materials from the element carbon, which, due to its active properties, permits the building up of an infinite variety of chemical compounds having highly varied properties. The name "plastics" has been applied to many of these products. The term "plastic" is rather difficult to define, but usually is applied to a group of materials, which, although stable in use at ordinary temperatures, are fluid at some stage in their manufacture, and can be shaped by the application of heat and pressure.

A good electrical insulator should possess the following properties: (1) Excellent insulating properties, (2) low water absorption, (3) nonflammability, (4) high heat distortion temperature, (5) high tensile strength, (6) good chemical resistance, (7) good dimensional stability, and (8) good fabrication properties.

Compounds containing only carbon and hydrogen have good electrical properties but are poor in regard to flammability, heat distortion, solvent resistance, and strength. The addition of polar groups, such as chlorine, hydroxyl, oxygen, and nitrogen, improves mechanical properties. Physical properties, such as crystallinity and cross linking, can also be employed. The best products are obtained by a compromise between electrical and mechanical properties.

The first plastic was a derivative of cellulose nitrate, but its advantages of solubility and ease of fabrication were completely offset by its high flammability. Other cellulose derivatives followed, among them cellulose acetate, cellulose acetate butyrate, and ethyl cellulose. The announcement by Baekeland in 1909 that the condensation product of phenol and formaldehyde would produce a moldable thermosetting resin gave the electrical industry products of great importance. Further research developed processes wherein the resin could be incorporated with many fillers, such as wood flour, cotton floc, rags, mica, slate, clay, asbestos, and glass, and also showed that these compounds could be molded by heat and pressure. Electrical properties were superior to the pure resin, and higher temperature limits were possible by the proper choice of fillers.

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Later, the impregnation of paper, linen, cotton, nylon, asbestos, and glass fiber with phenolic resin produced a wide variety of high strength laminates, which were very useful because of their ease of fabrication. Introduction of melamine resins, followed by the recent silicone resins, produced laminates with high arc resistance and low flammability. These laminates have great strength, especially those with glass fiber fillers. Development of the polyester resins made possible low pressure laminates, which can be produced in intricate shapes with very low mold pressure.

Wax is a good electrical insulating material, but for a long time its low mechanical strength and flexibility confined its use to impregnation of electrical insulation. Attempts to improve its properties led to the production of the vinyl compounds: vinyl chloride, vinyl acetate, and vinylidene chloride. The discovery of a method for polymerizing ethylene gave another compound for extrusion on wire in the same manner as some vinyl type compounds. For greater heat resistance, fluorine was substituted for hydrogen in ethylene, resulting in tetrafluorethylene, commercially known as "Teflon." These compounds failed to produce the properties desired for magnet wire insulation. Modification of polyvinyl acetate produced polyvinyl formal, which has good abrasion resistance and film strength. This compound is extremely useful for magnet wire insulation.

A whole host of rubber substitutes, neoprene, the Buna N and Buna S compounds, butyl and thiokol rubber, and the silicone rubbers, have been developed as a result of the limited supply of raw rubber. Each of these compounds has some useful and outstanding property which the electrical industry has used. Many miles of wire are covered by extrusion of rubber coats for protective coverings.

Attempts to improve amber led to the discovery of polystyrene, a material characterized by its exceptional dielectric properties, low water absorption, good dimensional stability and high optical clarity. However, a heat distortion temperature of 82°C and low impact strength have limited its usefulness in many electrical applications. The introduction of chlorine into the polystrene molecule forms a product known as "polydichlorostyrene," a compound of low flammability.

Another important class of organic insulator materials includes the natural fibers, cotton and silk. To improve their properties, the chemist has produced many synthetic fibers among them are the rayons, acetates, nylon, saran, orlon and dacron, each of which has outstanding advantages for the electrical industry.

The advent of electronic equipment and higher operating temperatures has called for a group of resins to improve the properties of the tars, pitches, and waxes. This group of resins, called "casting resins" or "potting compounds," includes the polyesters, the epoxy compounds, and the polyurethanes, each of which has electrical uses.

This article does not mention all of the plastic compounds available, nor many of the remarkable accomplishments in this new field which promise valuable developments in the future.

Vinyl Insulation

*J. R. Bukey**

In 1928, the vinyl resins began to appear on the market. Their versatility has resulted in a steady increase in production to reach an estimated 400 million pounds in 1951. Of this 400 million pounds of resin produced, a substantial quantity is being processed into vinyl insulation as extruded wire covering or calendered film for pressure sensitive or harness wrapping tapes.

Vinyl derivatives are basically those produced by the substitution of one of the hydrogens in ethylene by some other group. Thus, the vinyl radical is $CH_2 = CH-$. When a chlorine group replaces the hydrogen, the basic compound becomes vinyl chloride; analogously, the compound containing an acetyl group is vinyl acetate. When either of these basic compounds are polymerized alone or in combinations, the resulting resinous material is polyvinyl chloride, polyvinyl acetate, or a copolymer of polyvinyl chloride and acetate. There are numerous other substitutions and combinations possible, but for purposes of simplicity only, the polyvinyl chloride and polyvinyl chloride acetate copolymer will be considered.

A short time after the vinyl resins appeared on the market, the insulation chemist found that the hard horny thermoplastic polyvinyl resins had good electrical properties, but, as is so often the case, their physical and chemical properties would not permit their application without modification. This modification required that the resin be compounded with plasticizers, stabilizers, and fillers to give the desired physical and chemical properties to permit processing. In compounding polyvinyl chloride and copolymers of polyvinyl chloride acetate, a careful choice of plasticizers, stabilizers and fillers must be made in order that electrical properties are maintained. The plasticizers used are combinations of high boiling organic and inorganic esters chosen for their electrical stability and permanence in the compound. Since the compound will be subjected to high temperatures during processing and application, the resin must be stabilized against heat decomposition. This occurs when hydrogen chloride splits off the resin molecule. To stabilize the compound, it is necessary to add a hydrogen chloride acceptor which is chemically stable after having reacted with hydrogen chloride. Fine particle size inert fillers, usually clays, are added to the compound to give toughness, lower pound cost, and as a processing aid. The filler is chosen which adds the most to the compound with a minimum of degradation in electrical properties.

Vinyl insulation is presented to the trade in two general forms, that applied to wire by an extrusion process, or in tape form for use as pressure sensitive tape or harness wrapping tape. Some polyvinyl paste resins have been applied as potting compounds, but this usage has been small. The Underwriters' Laboratories have approved vinyl insulated wire for 60°C, types T and TW, and oil resistant, 80°C, types T and TW, radio hookup wire and oil resistant at 60°C, and 90°C and 105°C for radio hookup wire applications.

The first step in the preparation of compound for extrusion or calendering consists of loading the material components in a ribbon blender or double-arm mixer. These components include resin, plasticizer, stabilizer, filler, color, and lubricant.

* Firestone Plastics Company, Pottstown, Pennsylvania.

After a mixing cycle, the blended material is emptied from the mixer into a standard material drum which is conveyed to the loading platform of a banbury mixer, or an extrusion compounder. In either case, the pre-blend is fluxed into a plastic mass and thoroughly mixed to assure complete dispersion of the dry ingredients and complete solvation of the plasticizers. If a banbury has been used, the fused plastic mass is dropped onto a heated two-roll plastic mill. The plastic is stripped from the mill in the form of a ribbon and fed to a dice cubing device which cuts the ribbon into ¼ in. cubical pellets. The compounder-extruder is equipped with a multihole rod die and hence produces rods ¼ in. in diameter. The rods after cooling are fed to a high speed pelletizer where they are chopped into approximately ¼ in. lengths.

The prepared pellets of either type are fed to a crosshead extruder designed for the application of vinyl compound to wire. The extruder may be electrically or steam heated and have a delivery rate of 100 to 400 pounds of plastic stock per hour.

In the calendering operation, the pelletizing step is omitted and the strip from the two-roll plastic mill is fed to a four-roll plastic calender which forms the plastic mass into a sheet. Calendered sheets may range from .003 in. to .020 in. in thickness, and from 54 in. to 72 in. in width. This sheeting is wound into jumbo rolls preparatory to the application of a pressure sensitive adhesive and slitting to desired widths.

Several large manufacturers of insulated wire are now using dry powder blends in their extrusion process, thus eliminating the compounding and pelletizing steps.

Vinyl insulation is rapidly growing into one of the major consumers of vinyl resin and will be of greater importance in the insulation field as soon as use in heavier wire applications is approved.

Developments in the Mica Industry

*Moses D. Heyman**

Manufacturers of mica insulation are divided into two classifications, namely, block mica processors and built-up mica fabricators.

So dissimilar are these two branches of the industry that a firm engaging in one does not engage in the other, or if they do, the departments are kept separate.

Block Mica

Processing block mica involves splitting, cutting, or stamping pieces from a solid sheet or block of natural mica. There are in the United States approximately twelve concerns engaged exclusively in this business, some employing several hundred people. One concern manufacturing radio tube supports uses over 100 power presses in its daily production.

Up to the last quarter of the 19th century, block mica in this country and abroad was used mainly as stove windows. Following the invention of the phonograph and until 1922, the diaphragm and stove were its two most important uses in nonelectrical fields.

The employment of block mica in the electrical industry has resulted in a thriving business. When Edison produced his d-c motors and generators, he used Canadian phlogopite mica to separate the commutator segments, the pieces being hand cut from large sheets of block mica. Prior to 1920, condensers were made in fairly large sizes for wireless apparatus, and most of the good quality mica, aside from diaphragms, was used in the manufacture of condensers for magnetos. There are several concerns in the United States today normally using 100,000 lb or more of condenser splittings annually.

The electron tube was a great boon to the mica industry because it enabled the smaller sizes to be utilized. Radio tube supports are sometimes only ¼ in. in diameter, which enables nearly all sizes to be used.

About 300,000 lb of mica are used monthly for this purpose. Aside from condensers, most of the electrical mica consists of stained or partly stained material. Nearly all of this in size #6 is used for radio tube supports or washers. It is uneconomical to use a piece of mica that is smaller than one from which a ¾-in. disk can be cut.

Inasmuch as the percentage of mica over four square inches is less than five per cent of an average mine's production, it does not pay North Carolina and New Hampshire producers to operate a mica mining industry for such sizes only. Much of the production is mined by farmers in their spare time. Although there were many sporadic attempts to operate mica mines as a separate business, only a few of these were successful. The result is that recourse is made mainly to India, which has both of the indispensable qualifications for a mica industry, i.e., a substantial supply of the raw material, and a large amount of cheap labor.

The last fifty years has seen a fairly steady rise in the cost of all products. The price of mica up to the last seven years, however, has remained fairly constant. This was made possible by the following factors:

1. A large amount of small mica could be utilized as punchings for small parts.
2. The growth of the electrical industry made it possible for many of the smaller sizes and cheaper qualities to be sold at a profit.
3. The development of the splittings industry in India made possible built-up mica plate.
4. The extensive use of mica powder enabled a better price to be paid for scrap that previously could not be shipped profitably.

In 1938 the Army and Navy Munitions Board classified certain raw materials as "strategic." Mica was the only nonmetallic mineral that was given this designation. During World War II, the situation became extremely critical and even dangerous, so much so that the mica business was taken completely under the control of the Government, and a group of planes shuttled mica steadily from India to this country.

Further efforts were made to develop the mica mining industry in America; in fact, at one time a flat price of $6 per lb was paid by the Government purchasing agency for mica that previously could have been obtained for 30 cents, but even this failed to bring in a sufficient supply of material. A research program started with Government funds showed

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that unwarranted prejudice against certain types of mica, particularly in the field of films, existed.

Built-up Mica

In 1892, C. W. Jefferson and A. S. Dyer made the first built-up mica plate by splitting thin pieces of block mica and pasting them together with shellac. That same year a patent was granted to them, whereupon Mr. Jefferson left the Edison Company where he was employed, and together with others, began the manufacture of built-up mica products.

Today 85 per cent of all the mica manufactured in this country is made in this manner. It immediately gave rise to a complete new industry in India, the making of mica splittings, that employs over 70,000 people.

During 1950 the amount of splittings imported from India amounted to 22 million pounds, having a value of about $18,000,000. This was ten times the volume and five times the value of all block mica. However, nearly half of this went into the Government stockpile.

Improvements in built-up mica have been along two lines:

First, in manufacturing techniques, the most important was in the development of an automatic machine for lifting the mica flakes by vacuum and laying splittings down mechanically. This reduced the hand labor greatly.

Second, in materials engineering, the use of backing materials, such as paper, fiberglas, and various plastic sheets made it possible to produce flexible tapes for wrapping around coils. In this respect, a great improvement occurred in the types of adhesive used. While originally all the splittings were pasted with shellac or copal varnish, numerous synthetic resins are now in use, such as asphaltic compounds, silicone resins, and phenolics. However, the ones that seem to hold the greatest amount of promise are the solventless resins.

The manufacture of mica tapes and flexible sheets requires large size splittings and these are entirely made by hand, using female labor almost exclusively. The splittings themselves sell for as high as $6 per lb, with the result that micas of this type are very expensive. Such mica insulations come under "Class H" and up to the present time there are few substitutes. The situation is not a healthy one.

It must be considered that our huge electrical industry is entirely dependent upon India for its supplies of splittings. Prices are increasing steadily, and what is worse, the quality is getting poorer. As standards of living rise in India, the cost mounts, and the question arises whether India will not price itself out of the market. However, so far, that country has been able to sell all that it can produce, and buyers are apparently willing or must pay the increases. The number of importers compared with fabricators is out of all proportion to that existing with other raw materials. For example, there are practically as many importers as there are fabricators. Many of the latter do not import at all, but buy all of their stocks in this country from importers who are willing to take the attendant risks. Likewise, the lack of research and the paucity of new developments in this field are leaving it open to substitutes. Such attempts have been going on for nearly a century.

Integrated Mica

In 1940 the writer began to make a systematic study of the nascent forces holding the flakes of mica together to determine under what conditions the latter could be caused to recohere. This was followed by the development of different types of machinery and finally resulted in the production of a new material which is called integrated mica. The basis of this lies in the fact that if pieces of mica are split apart, they w recohere. However, the question of splitting them into e tremely thin flakes (most of which are less than four micro thick) without marring the surfaces was difficult. In 1942 t first disintegrator was built and worked successfully. report was made to the National Academy of Sciences August 1943 and the first patent was issued three yea later. However, the development of a complete automatica operated plant for producing integrated mica in continuo lengths took nearly six years longer.

Integrated mica is the only one of several materials recent developed that is really pure mica. It is likewise the on one that so far lends itself to being manufactured fro ordinary mine scrap. It is made in either muscovite phlogopite, and as it comes out of the sheeting machine it in the form of a sheet that can be made from .001-in. ¼-in. thick without laminating. In the pilot plant the sheet 12 in. wide and lengths of several hundred feet are readi made. The only products entering into its manufacture a ordinary mica scrap, (free from stones and dirt) and wate No adhesive is added into the product. Its dielectric consta approaches that of mica and its power factor is only slight higher than that of standard good-stained mica. Thus it suitable for certain types of condensers. The average dielectr strength of this material is about 400 volts per mil, A. C., cycles, but this can readily be raised to 1000 volts per mil b suitable impregnation.

Integrated mica is highly hygroscopic and lends itself impregnation with numerous resins. In an experimental wa it is already being used for radio tube supports, capacito and general electrical insulation. So far there have been n uses of built-up mica which integrated mica has not bee able to fill, and it undoubtedly will replace a large proportio of block mica now imported or mined in this country.

Samica

Samica is a trade name for a material that was develope in France. It consists of mica which has been dehydrated b heating it up to approximately 800°C and then beating it u in caustic while hydrochloric acid is added. The resultan combination liberates CO_2 and produces sodium chloride i the water. The former, with its bubbling action, helps th exfoliated mica to fall apart. After several washings, th material is run on a Fourdrinier paper machine and is forme in a sheet. About one per cent melamine resin is added to th mica pulp before rolling in order to keep it together. Com plete technical data on this product has not been available Due to the action of the hydrochloric acid on biotite an phlogopite, Samica can only be made in muscovite. Indi splittings or so-called factory scrap are the raw materia used. The maximum thickness at one rolling is about fou mils, but the mica can be built up to any suitable thickne by cementing these thin sheets together. This material ha been used in Europe and a factory is being built to produce i in this country.

Micamat

This is a product that has been developed by the Genera Electric Company, which is building a plant to produce it i Coshocton, Ohio. It is primarily designed to act as a surfacin material for use in mica tapes or built-up micas. Very littl technical information on this is available except for the fac that it is much like Samica. Its texture, however, appears t be finer. Its limitations apparently are the same as those fo Samica.

Feature Section

The Electrochemical Society—Past and Future

Presidential Address*

Ralph M. Hunter

We have already had sufficient of the past and the present to convince ourselves that the event which we are celebrating, was an important occasion. It is probable that none of the men present 50 years ago had any concept of its importance. Probably few of them realized that the Society which they were founding would continue for 50 years; further, few of them realized that the industries which they were establishing would continue to grow to the extent they have.

I feel duty bound to attempt to evaluate that first event, the present, and, I suppose, the future for the next 50 years.

The one difficulty with contemplation of the glories of the past is that we are appalled by the job before us if we even presume to continue the expansion which we have experienced. Certainly the founders were not appalled by the future. They were merely living and forging the tools which would enable them to live and to grow. Therefore, I would like to recreate, if I may, what were probably their thoughts and ideals 50 years ago and how they expressed them in their daily lives.

Many of my predecessors have referred with considerable profit to the messages of the Past Presidents. I do not intend to do this because it has already been well done, and because when most of them attained the presidency they had already achieved success and were looking back upon the significance of the Society to them, and thereby evaluated its contribution. Let us try tonight to consider what they did in the Society, with the Society, and for it, before they had attained their successes in it and in industry. In other words, how did they use this instrument which was forged 50 years ago, and in what way did this instrument contribute to their success?

It was an illustrious group. The charter membership list of this Society in 1902 is practically a Who's Who in the electrochemical and inorganic chemical industries in the United States; but most of them were unknown when they gathered together at 1409 Walnut Street, on April 3rd, at 8:00 P.M.; and remember that in addition to those whose names are on all our tongues, there are some whose names are not remembered for the success which they achieved.

On an early spring morning in 1902—if not the day of the founding, very close to it—I, your 49th President, was beginning my education in an experimental kindergarten about 2 miles from here, and I was expressing my fear of a spring thunderstorm, and disrupting the class by loud bawls every time the lightning flashed. It would be interesting to contemplate what would have happened if the teacher of that kindergarten class had called that charter gathering and informed them that here in the city where Ben Franklin had brought electricity to earth and defined its nature, the 49th President was disrupting kindergarten by his fear of electricity. If her call had been answered by a young man from Midland, Michigan, I can well imagine that he would have said: "Well, I am not particularly interested in what will be happening 50 years from now, because I am having considerable difficulty in satisfying my directors on what will be happening to me 3 years from now. Tell the youngster to learn what Ben Franklin and others have said about lightning and electricity; and, if he is able to continue, Professor Smith, of Case, has been discussing with Professors Burgess, Bancroft, and Richards what they believe should be taught about chemistry and electricity. If I am still in business after that youngster takes one of those courses, maybe I can give him a job. In the meantime I am trying to interest these young men here in a zinc-bromide battery somewhat similar to the Daniel Cell which I believe will revolutionize the battery industry; although yesterday several of them told me it had been patented by someone else ten years ago. By the way, you might mention to the youngster that Ben Franklin expressed some pretty good ideas on economics which will probably be as true 50 years from now as they are today."

If Charter Member H. H. Dow had depended upon his zinc-bromide battery alone for success, the youngster would not have been given a job.

Charles Acker described his plant at that first meeting. He produced 99.5 per cent NaOH, at 8,000 amperes and 7 volts, and current density of 19 ampere per in^2. This was one of the finest processes ever devised. Every young chemist should read Acker's paper of 1902. He was operating 45 furnaces on a molten salt cycle and claimed to have been continuously on the line from December 1900 to April 1902. His description of the method of starting is a masterpiece of simplicity. Truly he was years ahead of his time.

The first Secretary of the Society, C. J. Reed, was granted between 1902 and 1906 a group of patents on the mercury alkali chlorine cell, in which he, to a considerable extent, anticipated the development successfully accomplished after 40 years in the German cell.

Fortunately, many others, blessed with better timing, succeeded. Dow, Burgess, Becket, Whitney, Hall, Weston, and Acheson—each made his success in industry; Bancroft, Kahlenberg, Miller, Smith, and Richards in the academic

* Delivered at the Philadelphia Meeting, May 6, 1952.

field; Hering, Fitzgerald, and Addicks in the consulting field.

Chapter 10 in the "Life of Charles Burgess" (published in 1951) is labeled "Burgess and The American Electrochemical Society." It is a Presidential Address in itself. In it he recalled his meeting with Addicks, the many interests they had in common, and the friendship which grew out of it. The closing comment by Burgess, taken from his notebook many years later, must be quoted:

"I have a love for that Society. . . . I owe much to it, for it was a source of inspiration.

"I believe any young man ambitious to make a position for himself can do well to identify himself actively and consistently with a national organization bearing on his line of interest."

In their relationship with the Society these men were unconsciously creating one of the greatest tools which all of them used in their future scientific relations. As Burgess said, it was a source of inspiration to them, a group to which they could come for the exchange of ideas, and its membership was to them a reference book which they used in the solving of their many problems.

For 12 years I had the pleasure of working under Herbert H. Dow, and let me say that if one worked in the electrochemical division of The Dow Chemical Company in those days, one saw a great deal of the boss and heard a lot of electrochemistry. One also got a goodly measure of Dow's interpretation of Ben Franklin's philosophy on thrift and economics. During that time it is understandable that my contacts with other men in the industry were very few, primarily because we led an isolated life and I was a beginner in the company; but early in those years I was encouraged to join the Society and encouraged to attend its meetings. I know Dr. Dow valued it because on several occasions I have heard him, in discussing a certain research problem, say that the next time he saw Burgess he would ask him about it.

In advising me on graphite, he told me that he and Acheson had come to the conclusion that fine grinding was of great merit; Acheson had made a batch of graphite for him of which the raw material was procured by collecting the dust off the rafters in Acheson's petroleum coke grinding shed; they both agreed that it was the best graphite that Acheson had made, and that Dow had used.

In 1929 the Aluminum Company of America had reason to question the economic value of the Dow Magnesium Process and was tempted to use the German process competitively. It was interesting to note that Dr. Dow immediately thought of The Electrochemical Society and suggested that it would be agreeable to him to have Past President Fitzgerald evaluate both processes and that he (Dow) would be willing to stand by Fitzgerald's conclusions. During the years of their acquaintanceship in the Society he attained a great regard for Fitzgerald's integrity and economic astuteness.

The story of Acheson's life and his establishment of the Acheson Medal Fund, and the reading of the terms of the Weston Endowment for the Weston Fellowship bespeaks eloquently of the high regard in which these men held the Society, and their hopes that it would continue to serve future generations of electrochemists.

As so frequently happens in any group of aggressive individuals, time forces peculiar alignments. In a grim test of friendship in 1920 an interesting example occurred in which Past President Burgess found himself employed as an expert for a company against whom his friend, H. H. Dow, had brought suit for infringement. During my associations with the founder of our company, I had heard on several occasions references to this suit and to Dr. Burgess' participation in it.

It is indeed gratifying to read 30 years later Dr. Burgess' account of the incident. Both men preserved the highest regard for the other's scientific honesty and sense of fair play. It had no effect upon their friendship. This is an example of the type of professional relationship which the Society should endeavor to foster, and which should be the goal of all of us.

To those who may say that we are speaking of the giants of the men who were fortunate to live in the early days of this pioneer industry, let me give an example from my own experience.

In the early 1930's we were making strenuous efforts to redesign our magnesium cell to a reasonable size. One of the most difficult problems was a refractory which would stand chlorine and magnesium at the bath level at a temperature of 700°C. My Charter Member college professor, Albert Smith, of Case Institute, years before had impressed upon me the desirability of a cast-fused refractory for such difficult places and for sometime I had been trying to interest our members, who were connected with several refractory companies, in the problem. The Society met in Washington, D. C., in 1935, and one of the trips was to the Naval Academy at Annapolis, where the sightseers might visit the tomb of John Paul Jones, founder of the American Navy. I shall always remember this spot, not because of the Navy, but because between the gate of the Academy and the tomb of John Paul Jones, I was able to convince one of our members that we had a worthwhile problem. I know that I was successful, because a few weeks later Dr. Benner came to see us. On the occasion of his visit he made the optimistic remark that their company could cast anything that they could melt. They did. To that incident, I attribute a great deal of our success in supplying magnesium during the years 1941–45 to the excellent material which we were able to purchase from them.

And so, down through the years, to various people this Society has meant various things. We have grown in numbers, and yet we have remained a somewhat specialized group. Some sections of industry, wishing to become more specialized, have taken their specialization into new societies, but the interchange of the theoretical basic information has remained *here*, where it belongs. As the years have passed and as new uses of electricity to carry out or further chemical reactions have developed, this Society has adopted and encouraged these steps of progress.

Throughout these experiences, however, the objectives have not changed, nor will they change in the next 50 years. The exchange of information for the purpose of *improving* the theory, the engineering, and the production of electrochemical products, and the discovery of new products and new processes —these have been and shall be our goals.

It is the unique duty of the President at a significant anniversary to look into the future. It is unfortunate that your 49th Anniversary President is lacking in the ability to see far beyond the confines of earth and predict the grand scale which lies ahead. Possibly this is the effect of my early industrial training under H. H. Dow, who was always interested in the 5 years required from inception to production, and the 3 to 5 additional years which were required for profits. I suspect he knew that the tax collector would take care of the years beyond. Therefore, it may be necessary for you to wait for your 75th Anniversary President to obtain the long-range planning. However, I do believe that the future should be interesting.

Fifty years ago Charles Hall could have told you that he was producing about 7 tons of aluminum per day and it required the large sum of 6000 kilowatts. Probably no one in the secretive chlorine industry knew the total production, but it was in the neighborhood of 15 tons of chlorine per day, and required about 1500 kw. The combined requirements of these two industries were about 7500 kw.

Surely Charles Hall would have hesitated to predict that today the present aluminum production of the United States would require about 2,500,000 kw installed; and certainly none of the chlorine people would have foreseen that the same immediate plans call for 1,000,000 kw.

Now to use a familiar yardstick, the present capacity of all power stations in Niagara Falls, New York, is slightly under one-half million kw, or, if you wish to think of Bonneville Dam, it is also one-half million kw. Therefore, chlorine requires 2 Niagaras, and aluminum requires 5 Niagaras. But, what will happen if both of these products continue to grow during the next 50 years as they have in the last 50 years. Of course, anyone can predict that the power requirement will be large, and it will be.

If this growth should continue, chlorine will require 215 times as much power as it does today, or 430 Niagaras or Bonnevilles; and aluminum will require just slightly more. In other words these two industries will require one-half billion kw installed, or roughly 1,000 Niagara Falls. Would any one of you care to convert this to tons of coal per year?

Although there has been no indication of it in their past growth, I for one will predict now that this will *not happen*. The growth will indeed be tremendous, but not in these proportions. History shows that all industries tend to level out as they grow older, and, while each of these industries apparently shows no signs of having reached maturity, they undoubtedly will.

There are several reasons why such power demands will not materialize. In the first place, we will do our part to improve the efficiency of the several processes, and this will probably account for a considerable savings; but even more important will be the effect of substitutes, or even better products, to accomplish the same purposes with less expenditure of labor, equipment, and power. And this substitution and this improvement—and these new processes and products—are two reasons why the future for The Electrochemical Society should be bright. For those of you who are interested in power and its production, the mere thought of a fraction of the quantities I have mentioned indicates the importance of efficient power produced from any source, be it coal, gas, fission, or the sun.

There is still much to be done from the theoretical side. In his editorial published in the February issue of the JOURNAL, Dr. Harold Read makes the following statement:

"When one tries to describe how an ion is transferred from the plating bath to the lattice structure of the cathode one can speak only in the most general terms—terms which in no way give a clear picture of what is actually happening."

And, in the same issue, Past President Blum states: ". . . It may be safely stated that there is today no theory of the mechanism of electrodeposits that will even approximately explain existing knowledge."

Both of these comments are of interest to me, since I have discussed with several of the Sections the difficulties which we have in our attempts to study and explain the various reactions, ion speed, transfer number, and other phenomena peculiar to the diaphragms of the alkali chlorine cell.

In the Perkin Medal Address earlier this year, Past President R. M. Burns cites a beautiful example of one of the reasons why I do not believe that 50 years from now we will require 430 Niagara Falls' hydro plants to produce chlorine. Dr. Burns predicts a revolution in the electronics industry as a result of the developments of germanium, and quotes the tremendous reduction in size and power requirements for the transistor when it replaces the vacuum tube.

No, I do not dare to predict the exact future of power, chlorine, aluminum, or the electronics industry; but I do predict that chemistry, electricity, and engineering, if permitted to flourish in the American way, will produce enough power, enough chlorine, enough aluminum, and germanium—and a multitude of now unknown new materials and processes through industrial evolution—to satisfy and implement a growth of the same type as that of the past fifty years.

During the next 50 years, those of you who follow Richards, Burgess, Fink, Bancroft, and Smith will be called upon to educate the future members of our Society—our scientific posterity. You will also be called upon, and I suspect will need little urging, to write new laws, to find new ways of doing things, and even new products to make. Strange to say, I doubt if you will improve on Ben Franklin's ideas of thrift and economics. No one has.

Those who follow Hall, Acheson, Whitney, Tone, Dow, and Becket will be called upon to make more for less, to know more about how to do it, and to maintain the standard of growth which has become expected of the modern technologist. If we can make this Society the place where we bring our desires and ideas; if we can make our membership the group with which we discuss our problems; if we come to it for help; if we give what help we can to our fellow member; if that exchange of ideas is accompanied by a genuine and unselfish interest in the other's success, and the broadening of our own fields of knowledge and vision, I believe the next 50 years will be bright beyond our fondest wish.

The Founders[1]

Lawrence Addicks

Survivor is a word of rather ominous import. It is hard for me to realize that of the 350 enthusiastic and mostly young men who attended our first meeting only nine of us survive.[2] I am really here tonight as a sort of symbol—the fossil remains, in a reasonable state of repair, of an earlier age. I understand that, as a mark of respect, the usual after-dinner dance is to be forgone and you are to sing hymns instead.

I think, therefore, it is fitting to say a few words in defence of those days of sweet simplicity, before chemistry got fouled up with thermodynamics, while we still had the use of our legs, and when all good Philadelphians believed that when they died they went to Atlantic City.

Those of you who are old enough to have attended the early meetings will agree with me that we have lost some of the zest of the discussions which it would be well to try to recapture. We are so impersonal nowadays. I am sure Plato had to do a lot of editing on the Socratic dialogues before they were fit to send to his publishers. A paper submitted to the young Society was short and presented a problem or an idea for which the author was prepared to fight and probably had to. It was perfectly clear what he was shooting at. To be sure you generally thought he was a rotten shot and got up and said so. From then on out the meeting took care of itself. Now that was on a much higher spiritual level than pure science—it was FUN.

There was a much later type of paper that still turns up once in a while today. It is generally long, bristling with references, and deals with only a facet of a much larger subject not too closely related to the realities of life. After gazing at an x-ray picture of an electron crawling through a space lattice we older boys sit silent, wonder what the dickens it is all about, and just nod wisely. It is probably part of a doctoral thesis which the author has wrestled with until he hates the sight of it. A number of the younger auditors have strolled out during the recital and the chairman, who incidentally hasn't read the paper, adjourns the meeting for lunch. Now you can sit at home and read the printed paper. But the profit from a technical session is in the discussion. In our early TRANSACTIONS volumes the discussions sometimes covered more pages than the papers. Today we don't even transcribe them. Take a hand at tomorrow's sessions and see if you can't start an old-time scientific brawl. Make a few enemies—they are useful in forming character.

When this Society was founded it had two patron saints, a wise dualism. One was Willard Gibbs, all mathematical theory and no practical experience, and the other Michael Faraday, bottle washer to Sir Humphry Davy, all experimentation. The industrial foundations of electrochemistry were laid by electroplaters and such on a largely empirical basis. The phase rule worshipers looked down their noses at their uncultured associates, who in turn viewed the doctors of learning with what might be termed contemptuous awe. The apparently elementary problems of electroplating, by the way, have still not been dismissed as solved, as Doctor Blum and the Bureau of Standards will testify. While Gibbs and Faraday have long since learned to respect each other, the necessity for their philosophic accord still deserves to be kept in mind by the policy makers of the Society.

Another philosophical cleavage was social in nature. The Philadelphia circle embracing most of the founding fathers was steeped in dignity and protocol while the Niagara Falls coterie, rapidly expanding due to cheap local power, plus some far flung recruits even including one or two Quakers, believed in a more relaxed attitude toward life which finally found expression in what came to be known as Section Q, a most elusive fraternity somewhat along the lines of the famous Washington Gridiron affair. You can imagine the horror of Carl Hering, the embodiment of gentlemanly reserve, when two bribed New York City policemen and a couple of hired vaudeville actors staged a mock raid on the Chemists' Club in the middle of a technical session.

Then there was the job put up on Willis Whitney who, living in the Mohawk Valley, among his avocations developed quite a taste for hunting Indian relics. At a Niagara Falls meeting there was a picnic down the gorge and Whitney stumbled on a nice arrowhead. Later, his eyes on the ground, he found a couple more and was quite enthusiastic until a beautiful example turned up made of carborundum, after which he strangely lost interest.

Another device in keeping with Section Q traditions was to steal the notes of anyone scheduled to speak at a banquet and then organize a group to sit in a far corner and sing "Alouette" very quietly, watching developments while oxidizing alcohol. For the benefit of those who do not know French Canada, the lyrics of "Alouette" while starting out very innocently can, in the hands of the Niagara Section, become more of a lark than the title signifies.

I have two or three quaint memories of early members. Professor Richards, who did wonders in building up the Society (his students tell that it was wise to join if they wanted to be sure of graduating), liked to appear in remarkable gray frock coats, was also responsible for the glorious lilac bindings on our transactions, and to complete the picture kept a herd of St. Bernard dogs at his house on the Lehigh campus making it look like a Swiss hospice. I often recall Doctor Bancroft's saying plaintively: "You can never convince anbody with facts"—a remark of much wisdom. Doctor Baekeland, when we started to substitute a lantern for the blackboard, was not too much in favor of it. He said his experience in lecturing at Columbia was that when he turned the lights on again he found half his audience had sneaked out and the other half was asleep. I remember Doctor Roeber, that warmhearted, fussy little German, who, when he was given a nice build-up before being presented with an award, confessed that he was terribly embarrassed because his wife was sitting close at hand and she knew perfectly well that what had been said wasn't so.

All these men had much to do with the creating and nurture of this Society, but I cannot fail to include in any list the name of one of later vintage who for many years devoted to it untold service and energies, Dr. Colin G. Fink. Even he did not escape Section Q. I have indistinct memories of a plan to

[1] Address at the Fiftieth Anniversary Banquet of The Electrochemical Society, Philadelphia, Pa., May 6, 1952.

[2] It is now known that at least twelve charter members are living.—Ed.

present him with a leather medal for the least useful invention of the year in recognition of the really brilliant work he did on the electrolytic restoration of corroded ancient bronzes at the Metropolitan Museum of Art.

It seems to me that the greatest function of The Electrochemical Society is that of an interpreter, not only between Gibbs and Faraday, but in a much wider sense. At one of our very early meetings in Boston, Doctor Eliot, then president of Harvard, said that we were dealing with a "borderline science." I do not know exactly what he meant, but it gives me the cue I need to talk a little about the Tower of Babel, or in English, Babylon.

Several thousand years ago the Babylonians found out how to bake hard brick and tile and amused themselves seeing how high they could make their "ziggurats" as they called them. Accounts vary that heights from 300 to 600 feet were attained. The Hebrew moralist in Genesis takes the story from here and pictures Heaven in alarm at the presumption of man in reaching up toward the skies and as dealing with the problem by creating the famous "confusion of tongues". The masons could not understand the carpenters, the carpenters could not understand the laborers and so on, the result being the collapse of building operations and the putting of man in his place.

Now a similar situation has been building up. Starting with Aristotle's categories, man for centuries has been largely concerned in asking "what"? and has accumulated enormous lists of facts, until relatively recent times not knowing too well what to do with them. In the last hundred years or so research has centered on "how"? Then the geologists came along with "when"? And the philosophers still ask "why"? I don't know what heaven thinks of man's present presumption, but it almost seems as if the confusion of Babel is repeating itself. The chemists don't understand the biologists, the biologists don't understand the physicists, the physicists the geologists, the geologists the psychologists, the psychologists the economists, and the economists can't even understand each other.

Now, while The Electrochemical Society by definition merely stands between the chemists and the electrical engineers, in practice we seem to have become the homeland for the refugee scientists who find themselves in the misty no-man's land between the older disciplines. We are taking over rare metals, for example. Our opportunities are boundless—another thought for the policy makers.

When your president asked me to say what the English call a few "words," he was kind enough to state that I could talk about any subject that appealed to me as long as it was The Electrochemical Society and for just as long as I wanted, provided it wasn't more than 15 or 20 minutes, or delicate words to that effect. On the first count, aside from the Bible and a few minor matters, I have not strayed from the reservation. On the second I again have a thought to leave with you. How to choke off a speaker, be it from the banquet table, the pulpit or what have you, has long been as insoluble a problem of how to kill a government bureau once it has outlived its usefulness.

Many years ago I was the chairman of the New York Section of this Society; we had well attended meetings at the Chemists' Club, with a subject chosen in advance and several qualified men invited to discuss it, somewhat along the lines of the Town Meeting program on the radio. Of course the first man would way overrun his time and confuse everything. Well, we rigged a bright orange light on a fixture at the speaker's elbow and in view of the audience, telling him in advance that it would be lighted at the end of his alloted time just to keep him posted. When the light came on he would totally ignore it at first, but presently he would stumble over a word; next he would lose his place and finally mumble something and sit down. Psychologically he simply could not face that light and keep his attention on his speech. This device is the child of The Electrochemical Society and I should like to see it generally adopted.

I find that I spoke at the 25th anniversary dinner also. I hope it becomes habit-forming and you ask me to the 75th. You have a wonderful Society and, in the words of Tiny Tim, "God bless us every one."

MANUSCRIPTS FOR FALL MEETING

Manuscripts are now being received for the Fall Meeting of the Society, to be held at the Mount Royal Hotel in Montreal, Canada, October 26, 27, 28, 29, and 30, 1952. Subjects to be covered at the technical sessions will be Corrosion, Electric Insulation, Electrodeposition, and Electro-Organic Chemistry. To be considered for this meeting, triplicate copies of manuscripts or abstracts (not to exceed 75 words in length) must be received at Society headquarters, 235 West 102nd Street, New York 25, N. Y., not later than August 1, 1952.

Current Affairs

Commemorative Events and Largest Technical Sessions Mark 50th Anniversary Celebration

The Electrochemical Society celebrated its 50 years of growth and existence in its place of origin, Philadelphia, from May 4 to 8. Five days of divisional meetings, technical sessions, and social functions at the Benjamin Franklin Hotel broke all previous attendance records.

From the social and commemorative points of view, the reception for President and Mrs. Hunter and the banquet, in the Crystal Ballroom, were the high points of the meeting. Two of the original Charter Members attended the banquet. To Lawrence Addicks and G. H. Clamer this 50th Anniversary meeting recalled the first Society meeting on April 3, 1902 at the Manufacturers' Club. Dr. R. M. Burns read excerpts of letters from the ten other Charter Members, some of them indicating that, because of the effects of the years the banquet was commemorating, the trip to Philadelphia was not possible. Each of the twelve Charter Members received in person or by mail a scroll of Honorary Founder membership.

Both Dr. Addicks and Dr. Clamer accepted their scrolls personally and Samuel Sadtler's son received the scroll for his father. Dr. Addicks, speaking on behalf of the Founder Members, gave a most delightful as well as thought-provoking address. (See page 158C.)

Fifteen of the Society's Past Presi

Top row, left to right, Incoming President Warner receives congratulations from his predecessor, Dr. Ralph M. Hunter; Society officers, Warner, Hunter, and Linford are ready to comment on Dr. Burns' explanation; Dr. Lawrence Addicks and Dr. G. H. Clamer, representing the Charter Members, compare 1902 and 1952.
Center row, E. F. Kiefer and W. C. Moore are busy in the foreground, backed by J. C. Warner and J. W. Marden; the Society's Secretary and a croupier discuss the finer points of the game to the amusement of Mrs. Kiefer, A. T. Hinckley, M. J. Udy, D. S. Carr, Mrs. Linford, Dr. Moore, and F. C. Mathers; E. G. Enck provides local color as the dapper gambler of earlier times; A. L. Ferguson and his fellow players add a number of Watts to their collections as Mrs. Colin G. Fink considers her next move.
Bottom row, G. W. Heise smiles while C. A. Hampel places some Watts; players from F. A. Lowenheim to Dr. Addicks watch Croupier Lukens at the wheel of fortune; scene at the reception for Dr. and Mrs. Hunter before the banquet.

dents attended the banquet in honor of this special occasion. Past President Faust called the roll of his predecessors, first asking that applause be delayed until he had named them all, but as each Past President rose from his seat at the head table there was a spontaneous round of acknowledgment.

The roll called included: Lawrence Addicks, A. T. Hinckley, H. C. Parmelee, William Blum, Bradley Stoughton, H. S. Lukens, James H. Critchett, Duncan A. MacInnes, H. Jermain Creighton, F. C. Mathers, R. M. Burns, S. D. Kirkpatrick, W. C. Moore, George W. Heise, A. L. Ferguson, and Charles L. Faust.

Dr. Ralph Hunter as outgoing President delivered the presidential address (see page 155C) and incoming President Warner acknowledge his new office with brief, humorous remarks on the indispensability of the individual.

One of the special features of the 50th Anniversary meeting was the signing by many members of a scroll to be presented to Dr. Colin G. Fink in appreciation of his many contributions to the Society.

Wednesday evening's entertainment, following a buffet supper, was a "Las Vegas" night. Incredible amounts of "Watts," the "Elektrokomical Kash" that was legal (?) "tinder" for the evening, exchanged hands over the tables. The players were then exposed to a talk based on the fact that crime does not pay, followed by the drawing of door prizes ranging from shoe polishing kits to fine luggage.

Technical sessions proved worthy of the semicentennial event. Meeting rooms were well filled for all symposia and to overflowing for some sessions. The special round table on the teaching of electrochemistry resulted in considerable discussion from the floor and will be written up in detail in a later issue of the JOURNAL.

The Electric Insulation Division produced sessions of widespread interest, including several papers on nonwoven fabrics, their development and applications. Although the number of papers on instrumentation was small, comparatively speaking, there was no lack of interest and discussion. Theoretical Electrochemistry sessions produced prolonged and detailed discussion on new ideas on which many listeners withheld decision. Boron, gallium, and zirconium, among other metals, received the attention of men interested in rare metals and the phosphors, including trapping phenomena, properties, cathodoluminescence, etc., held the interest of the luminescence group. Screen application papers were well worth the trip to the Harrison Laboratory. Members will doubtless be interested in more information on the sign convention discussion which will be published in a later issue of the JOURNAL.

The program planned for the ladies while their men were attending sessions was highly successful and included diversified activities to appeal to various tastes. Highlight of their special program was the trip to Bryn Athyn Cathedral and luncheon at the Huntington Valley Country Club, involving a bus trip the ladies are apt to recall vividly.

The Philadelphia Section, host for the meeting, organized and planned a program that ran with precision and smoothness. General Chairman H. S. Lukens and his committeemen earned the thanks and congratulations of the 672 members and guests who enjoyed one of the finest and most successful meetings ever held by the Society.

Awards of Young Author's and Turner Book Prizes

JOHN T. BYRNE receiving award from DR. HUNTER

The Young Author's Prize of $100 was awarded to John T. Byrne of The Dow Chemical Company, AEC Rocky Flats Plant, Denver, Colorado, for the paper entitled "Critical Interpretation of Electrodeposition Studies Involving Traces of Elements," of which he was co-author with L. B. Rogers. This paper was published in the November 1951 issue of the JOURNAL.

Dr. Byrne received his Bachelor of Science degree in chemical engineering from Tufts College in 1948 and the Ph.D. degree in analytical chemistry from Massachusetts Institute of Technology in 1951. His graduate work, on the electrodeposition behavior of traces of elements, was done under Professor L. B. Rogers. Since June 1951 Dr. Byrne has been employed by The Dow Chemical Company. His chief interest is in analytical methods development.

The Turner Book Prize of $50 worth of scientific books, published by Reinhold Publishing Company, was awarded jointly to Kurt H. Stern of Clark University, Worcester, Massachusetts, and Charles C. Templeton of Shell Oil Company, Houston, Texas. They were

KURT H. STERN

co-authors of the paper "The Electrical Conductance of Solutions of Cobalt (II) Nitrate Hexahydrate in Acetophane at 25°C," which appeared in the JOURNAL in November 1951. The work was part of a program sponsored by the Atomic Energy Commission at the University of Michigan.

Mr. Stern received the A.B. degree from Drew University in 1948 and the M.S. degree from the University of Michigan in 1950. Here, while taking a course in electrochemistry from Professor Ferguson, he became interested in the theory of electrolytic solutions. He is at present completing requirements for his doctorate at Clark University.

CHARLES C. TEMPLETON

Dr. Templeton received the B.S. degree from Louisiana Polytechnic Institute in 1942 and, after service in the Navy, took the Ph.D. degree from the University of Wisconsin in 1948. For

the next two years he was an instructor in physical chemistry at the University of Michigan and, in 1950, joined the Exploration and Production Research Laboratory of Shell Oil Company. His research interests include the study of water-metallic nitrate-organic solvent systems, and multiple fluid flow through porous media.

The awards were formally presented by President Ralph Hunter at the Philadelphia meeting.

Highlights of Board of Directors' Meeting

(Held May 4, 1952)

The Board approved the action of the Membership Qualifications Committee in electing the members whose names were recommended during the months of February, March, and April.

The Board gave approval to the proposal made by the Ashley-Ratcliff Corporation of New York to microfilm the first three volumes of the TRANSACTIONS of The Electrochemical Society, and also to reproduce, in full size, the first and the third volume. The Society will receive a 10 per cent royalty.

Due to the recent death of Francis Mills Turner, the Turner Book Prize, which has been a personal undertaking of Mr. Turner, would have terminated automatically had it not been for the action of Mr. Fred W. Peters, Vice-President of Reinhold Publishing Corporation, in underwriting the prize for the year 1951. In order that this prize might continue, Mr. Peters had previously informed the Secretary that the Board of Directors of Reinhold Publishing Corporation had offered to continue this prize in a slightly different form. The award would be increased to $100 retail purchase value of technical books of any publisher. The award would be administered as at present by the Society. Reinhold would simply arrange to obtain the $100 worth of books for the award winner after he forwards his selections. On motion of Dr. J. C. Warner, it was voted that we accept the Reinhold offer and suggest to Reinhold that they choose the name of the award since Mr. Peters had submitted two alternative wordings.

John T. Byrne was awarded the Young Author's Prize and the Turner Book Prize was awarded to both Kurt H. Stern and Charles C. Templeton for their joint contribution.

The Secretary reported the marriage of our past Managing Editor, Miss Eleanor Reid, to Brian Derek Forrow, and read a note of appreciation received by Dr. Burns for the gift presented to her in the name of the Board of Directors of the Society.

R. M. Burns, reporting for the Publication Committee, presented a good many figures with respect to the JOURNAL, showing distributions of technical papers through divisions and also a breakdown of number of pages of Technical Reviews, Current Affairs, Editorials, etc. Dr. Burns then introduced Mrs. Ruth Sterns, our new Assistant Editor, and also presented the resignation of Mr. Frank LaQue, who has been advised by his doctor to relinquish his duties. Mr. LaQue's resignation was regretfully accepted with a unanimous vote of appreciation for his services during the past years.

A. W. Whitaker, General Chairman of the Montreal Meeting, gave a report on the plans for this meeting. Of outstanding interest to the members is the proposed trip to Arvida, leaving Wednesday evening by rail, arriving in Arvida Thursday morning. The day will be spent viewing the aluminum reduction works and auxiliary installations, and the return will be made to Montreal during Thursday night.

Harry R. Copson, General Chairman of the New York Meeting, made a request that the Richards Memorial Lecture be held at the New York meeting next spring. This request was granted, and the Local Committee was directed to make nominations to the Board of Directors for suitable candidates for the lecture.

C. L. Faust, reporting for the Ways and Means Committee, requested that the Board establish the policy that sustaining members receive one copy of the JOURNAL. This was approved.

The following schedule of meetings was approved as recommended by the Ways and Means Committee:

Fall of 1952 —Montreal
Spring of 1953—New York
Fall of 1953 —Wrightsville Beach
Spring of 1954—Chicago
Fall of 1954 —Boston
Spring of 1955—Cincinnati
Fall of 1955 —Pittsburgh
Spring of 1956—San Francisco
Fall of 1956 —Cleveland

L. I. Gilbertson reported on the activities of the Membership Committee, showing that our Society is continuing to grow in numbers.

Walter H. Prine, Chairman of the Sustaining Membership Committee, reported that since the Detroit Meeting the following companies have taken out sustaining memberships:

Air Reduction Company
American Potash & Chemical Co.
Armour Research Institute
E. I. du Pont de Nemours & Co., Inc.—Screen Division
Eagle-Picher Company
Kaiser Aluminum & Chemical Co.
McGean Chemical Company

Fred A. Lowenheim reported for the Local Section Advisory Committee, and requested that monies be made available to those interested in forming new sections. The particular case in point are the Indianapolis members who are, at the present time, considering the formation of a section. On motion of Dr. Warner, it was voted to advance up to $25 against the first year's allotment of $50 for sections holding four meetings a year. In this fashion, money could be made available to hold an organization meeting at which time collection of local section dues might begin.

Under old business, the Board discussed the matter of increasing the dues and subscription rates. It was voted that these rates be increased 25 per cent starting January 1, 1953.

At the conclusion of the Board meeting the new President, Dr. J. C. Warner, called a meeting of the new Board of Directors into session. The first item of business was a resolution of thanks for the services of Dr. Ralph Hunter as President during the last year. Acting under the Constitution, the Board then appointed Henry B. Linford as Secretary.

The next meeting of the Board of Directors was called for Friday, June 27, in the Society office, 235 West 102 Street, New York 25, New York.

HENRY B. LINFORD, *Secretary*

Report of Tellers of Election

For President: J. C. Warner 701; 7 write-ins; 20 abstentions.

For Vice-President: Kenneth Compton 142; Sherlock Swann 227; Herbert H. Uhlig 356; 2 write-ins; 1 abstention.

For Treasurer: E. G. Widell 697; 3 write-ins; 28 abstentions

(Signed): Herbert P. Dengler, *Chairman*
Irving Moch
David Feder
Tellers of Election

New Developments Noted at Sixth Annual Battery Conference

A large contingent of the Battery Division of The Electrical Society attended the Sixth Annual Battery Research and Development Conference, held at the Berkeley-Carteret Hotel, Asbury Park, New Jersey, May 13 and 14. Division members actively participating in the conference were: William Shorr, Roy C. Kirk, Richard Clune, Joseph C. Schumacher, Bernard Agruss, U. B. Thomas, Arthur Daniel, Eugene Willihnganz, Arthur Fleischer, E. J. Ritchie, Judson West, Jr., A. B. Garrett, and David Linden.

A discussion in progress at the conference (*left to right*): Grenville B. Ellis, Chief, Power Sources Branch, Signal Corps Engineering Laboratories; Gordon McRea, Vice-President, Bell Telephone Laboratories, guest speaker; Major General Kirke B. Lawton, Commanding Officer, Fort Monmouth, New Jersey; and Colonel Edwin R. Petzing, Director, Signal Corps Engineering Laboratories.

The conference is sponsored each year by the Signals Corps Engineering Laboratories, Fort Monmouth, New Jersey, under the direction of Grenville B. Ellis, Chief, Power Sources Branch. The recent meeting attracted more than 300 representatives of the battery industry, which included over 150 government and commercial groups.

Highlighting the meeting was the announcement by the Signal Corps Engineering Laboratories of the development of a new line of special purpose "one-shot" batteries for use with guided missiles, pilotless aircraft, rockets, and similar equipments, the size and weight of which are only one-third that of the more conventional type batteries previously employed for these applications. Also, further details were announced on the magnesium battery which recently has been developed and which will out-perform the conventional zinc-type battery, giving more than twice its capacity. This cell is particularly desirable since it utilizes noncritical materials in place of zinc. Recently the Signal Corps Engineering Laboratories have procured magnesium batteries for test over wide temperature ranges and various capacities prior to their adoption for field use.

Gordon W. McRea, Vice-President, Bell Telephone Laboratories, the luncheon speaker, gave a very enlightening talk on transistors and some of the more recent applications in replacing the vacuum tube. The battery industry is particularly interested since transistors are capable of low power operation and so would open an entire new field of applications for batteries.

Four symposia were presented in the two days; these covered recent and proposed battery research, dry cell batteries, secondary batteries, and batteries with special applications.

Battery Research

At the morning session on May 13, Herbert A. Gottschall, Markite Company, spoke on the recent development of a leakproof plastic miniature battery using a conductive plastic construction. It was pointed out that this encapsulated structure is particularly desirable for the alkaline dry cells designed to give long life, high voltage, and low drain characteristics.

Also under investigation is the development of a new absorbent and film type of battery separator having better properties than those currently used. Paul F. Bruins, Polytechnic Institute of Brooklyn, presented a paper on recent work done with resin bonded nonwoven textiles made from synthetic fibers and the production of microporous films of chemically resistant resins. Many other new separator materials are in the process of evaluation at this time.

At the close of the morning conference, William Shorr, Signal Corps Engineering Laboratories, described several new phases in the SCEL battery research program. Quantities of radioactive waste materials and their possible use in high potential power supplies has opened an entire new field of exploitation, since the shelf life would be of such a magnitude that the battery should remain relatively unaffected for decades. The life of a device wherein portable electrical energy is derived from nuclear energy would chiefly be a function of the half-life of the radioactive material. Also radioactive tracer techniques are now being employed for the elucidation of electrode reaction mechanisms of batteries over various operating conditions.

Dry Cell Batteries

During the afternoon session, Dr. Roy C. Kirk, Dow Chemical Co., pointed out that the magnesium-manganese dioxide dry cells have given successful shelf life up to 3 years, and at high drains were capable of capacities considerably greater than the standard Leclanché cell. Also, new intercell connection techniques have been improved. A wax-powdered graphite mixture offers considerable promise as a conductive anode coating in flat cell pack construction.

W. B. Woodring, Olin Industries, Inc., reported progress on the development of a nonreserve type battery that will operate at temperatures as low as −65°F. A study of electrolyte composition indicated that a lithium chloride-zinc chloride-amonium chloride-water electrolyte is satisfactory at −40°F. Further experiments have revealed that an electrolyte system of lithium chloride-zinc chloride-water is best suited for work at −65°F. Mr. Woodring also pointed out that storage temperature appears to have an important effect on delayed low temperature discharge.

Better delayed results are obtained from cells stored at 0° than from those stored at 70°F when they are tested at −65°F.

Joseph Dalfonso, P. R. Mallory & Co., Inc., spoke on the standard alkaline dry cell design and its possibilities in low temperature application. Mr. Dalfonso reported that the present design is unsuitable to operation at extremely low temperatures since electrode polarization, particularly at the anode, was found to be the prime controlling factor in low temperature operation. Relatively large electrode areas and close electrode spacings along with a considerable size increase would be required to maintain a discharge capacity equivalent to that normally obtained at room temperature. On the other hand, with retention of established cell sizes, a substantial reduction in room temperature capacity would be required to obtain optimum low temperature operation.

The second session of the Dry Cell Battery Symposium was devoted to the presentation of several papers on the alkaline dry cell batteries and the successful production of battery-active manganese dioxide from domestic, low-grade, natural manganese ores. Richard Clune, P. R. Mallory & Co., Inc., reported on the successful development of a miniature alkaline dry cell capable of high drain operation over a range of operating temperatures. Cells were developed in two sizes, namely 150 and 50 ma hr, which would be capable of delivering rated capacities on discharge rates of 5 to 20 hours at room temperature.

In the report on the refinement, by electrolytic process, of manganese ore, Joseph C. Schumacher, Western Electrochemical Company, pointed out that the pilot plant has been in operation for over twelve months and the product quality far exceeds Signal Corps specification requirements. Plans are now in progress to expand the present plant capacity tenfold to meet the ever-increasing demand for the product.

Secondary Batteries

Tellurium-Silver Alloy Grids: The program on secondary batteries was opened by Bernard Agruss, National Lead Company, who discussed the development of corrosion-resistant positive grids by small additions of silver and tellurium. These grids when incorporated into batteries have shown a minimum of 100 per cent more life than the conventional antimonial-lead grid on overcharge tests.

Plated Aluminum Grids: L. L. Carrick, University of Michigan, and Eugene Willihnganz, Gould-National Battery, Inc., discussed the use of lead-plated aluminum grids in the conventional lead-acid type battery. Dr. Carrick stated that the process of lead plating of aluminum grids has been shortened and improved to the extent that it may be adopted to production line operation. Dr. Willihnganz agreed that the lead-plated aluminum grids had excellent shelf life and high discharge characteristics, but, however, also stated that the expected saving in weight could not be obtained. The lead-plated aluminum grids were heavier and contained less active material than an equivalent sized cast lead grid. This increase of weight is the result of two factors—punching operations of aluminum and thickness of plating. The improvement in grid conductivity resulting from the presence of aluminum did not balance the loss of active material content except when the discharge rate was great enough to exhaust the battery capacity in 0.5 minutes or less.

Special-Purpose Batteries

The second day of the conference, M. F. Chubb, Eagle-Picher Company, reported on the new water-activated cuprous chloride-magnesium system. It has developed particular interest because of its ease of activation, adaptability to high voltage construction for "B" batteries, and general rating as a high capacity, low weight, moderately priced, expendable power source. Although developed only recently, this type of battery is at the present time in large scale production for several meteorological applications and promises to spread to other fields in the near future. The cuprous chloride-magnesium battery is particularly desirable because of its most effective use at discharges from approximately the 1 to 4 hour rates, and where advantage can be taken of the excellent low temperature characteristics of the battery because of its highly exothermal discharge reaction.

In the discussion of the zinc-silver peroxide system, N. T. Wilburn, Signal Corps Engineering Laboratories, stated that the high power output per units of weight and volume and constant voltage at high rates of discharge lend the system ideally to specific high rate military application where strict voltage regulation is required and where space and weight are critical factors. A standard line of such batteries is now in production and has been procured by the Signal Corps for missile application and extensive testing.

Work is now being done to create a nonreserve type zinc-silver peroxide battery capable of one year shelf life at 80°F retaining most of the good characteristics of the present reserve-type battery. Since no activation would be necessary for this type of battery, requirements of many new missile applications, such as defensive missiles, can be met.

International Committee to Meet in London

The fourth meeting of the International Committee of Electrochemical Thermodynamics and Kinetics (CITCE) will be held in London (Imperial Institute of Science and Technology) and Cambridge (Cambridge University), England, on September 10 to 13, 1952. A number of laboratories specializing in electrochemistry and corrosion will be visited by the participants on September 8 and 9. Information concerning this meeting can be obtained from Dr. Marcel Pourbaix, Secretary General of the Committee, University of Brussels, 50 Avenue F. D. Roosevelt, Brussels, Belgium, or from Dr. T. P. Hoar, Vice-President of the Committee, Department of Metallurgy, Cambridge University, Pembroke Street, Cambridge, England.

Previous meetings of CITCE were held in Belgium at Brussels in March 1949, in Milan, Italy, and vicinity in September 1950, and in Bern, Switzerland in August 1951. Members of the Board holding office until the end of the fourth meeting are: P. Van Rysselberghe, University of Oregon, President; T. P. Hoar, Cambridge University, and R. Piontelli, Politechnico of Milan, Vice-Presidents; M. Pourbaix, University of Brussels, Secretary General; E. Lange, University of Erlangen. Fifteen countries are represented in the membership of nearly one hundred. In each of these countries a national secretary attends to all matters pertaining to the activities of the Committee and represents his country in the Council.

Proceedings Available

The Proceedings of the second meeting have been published by the Tamburini firm of Milan. They may be ordered from Dr. Marcel Pourbaix at the address given above. The price of $6 can be paid directly by personal

check. A reduction of 20 per cent, making the price $4.80, is granted to the members of The Electrochemical Society and/or of the National Association of Corrosion Engineers. The proceedings of the third meeting are being published by the Manfredi firm of Milan and will appear shortly. Orders may be placed with Dr. Pourbaix.

Chicago Section Presents Program at ACS Meeting

In response to an invitation from the Chicago Section of the American Chemical Society to participate in its April 6th meeting, the local section of The Electrochemical Society presented a panel discussion entitled "This is Electrochemistry!" The subject covered a discussion of the status of electrochemistry—in celebration of the 50th anniversary of the founding of the Society.

Taking part in the panel were: F. J. Kirkman who spoke on "Batteries" Ray I. Lindberg, "Corrosion"; Clifford A. Hampel, "Industrial Electrochemical Products"; and O. W. Storey, moderator. The meeting was deemed a successful one, and the Society members wish to express their appreciation to the Chicago Section of the ACS for the opportunity of presenting this program.

O.W.S.

Proposed Trip to Arvida during Montreal Meeting

The Montreal Local Committee has proposed a trip to the plant of Aluminum Company of Canada, at Arvida, in connection with the fall meeting of the Society. Arrangements will be made to leave Montreal by train on Wednesday evening, October 29, and arrive in Arvida Thursday morning, spending the day at the plant, and returning to Montreal Thursday night.

Reservation cards and details of the arrangements for the trip will be sent to members with the Program Booklet for the fall meeting so that those interested may communicate with the local committee as early as possible.

Revised Montreal Meeting Dates

The dates for the Montreal meeting of The Electrochemical Society have been revised as follows: *the meeting will begin on Sunday, October 26, and continue through Thursday, October 30.* This moves the meeting forward one day from dates previously scheduled.

Conserving Our Most Critical Resources

With the mounting defense program, the rapid increase in industrial production is being accompanied by a rising industrial accident rate. The pattern is much like that of the early years of World War II. Not until 1943 was the upward trend halted by intensified safety programs. In the interest of conserving that critical, irreplaceable resource, manpower, the Mine Safety Appliances Company has published a booklet calling attention to the need for reappraising and strengthening existing safety programs. Copies of "Conserving Our Most Critical Resource" may be obtained on request to Mine Safety Appliances Company, Braddock, Thomas and Meade Streets, Pittsburgh 8, Pennsylvania.

Electroplaters' New Address

The executive office of the American Electroplaters' Society was moved from Jenkintown, Pennsylvania, to the American Building, 445 Broad Street, Newark 2, N. J., on April 1. At the same time the editorial and business offices of *Plating* also were moved to Newark. A production office has been established at 5800 N. Marvine Street, Philadelphia, to which plates, cuts, and production correspondence should be directed.

News From the Divisions

Electronics Division

At the Philadelphia meeting in May, the Electronics Division presented symposia on Luminescence, Rare Metals, Instrumentation, and Screen Application and held a joint session of the Rare Metals Group and the Electrothermic Division. Chairmen of these symposia, Roland Ward, D. M. Wroughton, R. H. Cherry, C. W. Jerome, and A. E. Hardy, are to be commended on an excellent job of preparing the sessions and arranging to get the papers.

It is expected that the 1953 spring meeting will include symposia on Luminescence, Rare Metals, and some phase of general Electronics as has been the practice for the past four or five years.

The new officers elected at the Philadelphia meeting were:

Chairman—J. R. Musgrave
Vice-Chairman, Luminescence Group—A. L. Smith
Vice-Chairman, Rare Metals Group—D. M. Wroughton
Vcie-Chairman, General Electronics Group—Meier Sadowsky
Secretary-Treasurer—C. W. Jerome

* * *

Screen Application

A group of workers in this field approached the Electronics Division prior to the Washington meeting in April 1951, asking that they be sponsored for their symposia and round tables. The Executive Committee at that time agreed that they should be sponsored on a trial basis. Since that time, this group has had two symposia, one at the Fall meeting in Detroit and another during the spring meeting in Philadelphia. Contingent on Society approval, they have now been accepted in the Division.

Abstract Booklets

The suggestion was made at the 1951 spring meeting that a booklet of extended abstracts or condensed papers be published under the auspices of the Electronics Division. After much preliminary work the project was submitted to the Society Board of Directors in October and permission was granted to publish such a booklet.

This project was financed by dues from the membership and eventually it was found possible to name a price of $1.50 for the booklet. Prepublication orders were in the hands of the members before the Philadelphia meeting and copies of the abstract booklet were on sale at the registration desk.

The membership of the Electronics Division and the Society have decided, from this year's experience, to continue this practice.

Anniversary Issues

In connection with the 50th anniversary of the Society, special issues of the JOURNAL were assigned to each of the Divisions; the Electronics Division was given the April and May issues. Dr. John W. Marden supervised and edited the anniversary features which were presented in these two issues, as well as writing much of the historical material himself. Rudolph Nagy, Martin F. Quaely, G. A. Perley, and R. H. Cherry all presented review articles on the Division's accomplishments during the past 50 years. Dr. Lawrence Addicks wrote an editorial on rare metals and

other members of the Division contributed with write-ups and criticism.

Membership

Approximately 225 members were listed as of May 1, 1951. Subsequent additions to our membership have raised this total to 276 as of March 5. Only a few members were lost by resignations on the first of the year.

Under the chairmanship of L. I. Gilbertson, the Membership Committee of the Society has been extremely active. The increase of members within the Division has been due in some part to the activities of the Membership Committee, but a large portion of the credit for increased membership in the Electronics Division should go to the divisional officers who individually canvased each prospect submitted to them.

Although we have 276 members registered with the Society as belonging to the Electronics Division, only 91 of this group paid dues. This is but one-third of the membership. It is hoped that a better response will be encountered this year if it is found necessary to assess dues again.

Electro-Organic Division

The following candidates have been nominated and the nominations accepted for election at the meeting of the Electro-Organics Division, to be held during the fall meeting of the Society in Montreal:

Chairman—Christopher L. Wilson
Vice-Chairman—Harold M. Scholberg
Secretary-Treasurer—Stanley Wawzonek

The above slate was submitted by the nominating committee: Sherlock Swann, Jr., Chairman; N. M. Winslow and H. J. Creighton, members.

H. M. SCHOLBERG, *Secretary-Treasurer*

Electrothermic Division

The annual luncheon and business meeting of the Electrothermic Division was held Thursday, May 8, at the Benjamin Franklin Hotel in connection with the Spring Meeting of the Electrochemical Society, with Dr. C. H. Chappell, the Division Chairman, presiding at the business meeting.

Dr. Chappell expressed the appreciation of the Division for the work which Guy Fetterley had done as Program Chairman during the past year, and for the work of Julian Glasser in organizing the Electrothermic Division's contribution to the Anniversary Issue of the JOURNAL.

The meeting was adjourned after the report of the Secretary-Treasurer, and a report on the progress of the Division's major project, the compilation of a monograph on refractories.

No election was held at this meeting, since the officers of the Division are now elected for a two-year term. The next election of officers will be in connection with the 1953 Spring Meeting.

I. E. CAMPBELL, *Secretary-Treasurer*

Industrial Electrolytic Division

The meeting of the Industrial Electrolytic Division, in Philadelphia, May 5th, was called to order by the Secretary-Treasurer, Kenneth B. McCain. The minutes of the preceding meeting and the reports of the Secretary and Treasurer were read and accepted as read. The nominating committee consisted of M. S. Kircher, Chairman, R. B. MacMillin, and James King. Their report, presenting the nominations listed below, was read by Mr. King:

Chairman—Dean O. Hubbard, Hooker Electrochemical Company, Niagara Falls, N. Y.
Vice-Chairman—Fred W. Koerker, Dow Chemical Company, Midland, Mich.
Secretary-Treasurer—A. R. Orban, Niagara Alkali Company, Niagara Falls, N. Y.

No further nominations were made from the floor and the above slate of officers was unanimously elected.

The Chlor-Alkali report was read by Warren Sherrow and copies of the report will be sent to members of the Division.

During a discussion it was brought out that more papers will be needed for the Fall Meeting at Montreal. No new business was introduced, and the meeting was adjourned.

KENNETH B. MCCAIN
Secretary-Treasurer

PERSONALS

WILLIAM J. ROSENBLOOM of Chemical Construction Corp., New York, N. Y., has transferred to the company's Canadian office, Chemical Construction (Inter-American) Ltd., 74 Wellington St., West, Toronto, Canada.

WILLIAM P. INNES has accepted the position of Technical Director, MacDermid, Inc., Waterbury, Conn. Mr. Innes was formerly research engineer in the Research Laboratories Division, General Motors Corp., Detroit, Mich.

WILLIAM B. ROBERTS has left Sylvania Electric Products, Inc., Flushing, N. Y. to become Chief Research Chemist for Sarkes Tarzian, Inc., Rectifier Division, Bloomington, Ind.

ROGER G. SWEET of Kennecott Copper Corp., formerly of Bexley, Ohio, has been transferred to the company's office at 161 East 42 St., New York, N. Y.

GEORGE GLOCKLER, Department of Chemistry, State University of Iowa, Iowa City, has joined the Ordnance Research staff of Duke University, Durham, N. C.

J. R. SMITH, The Electric Storage Battery Company, Philadelphia, Pa., is now located at this company's plant in Fairfield, Conn.

LYLE I. GILBERTSON is now at Air Reduction Company, Inc., Research Laboratories, Murray Hill, N. J. Mr. Gilbertson was previously at Airco's New York office.

NATHANIEL HALL, Consulting Engineer, formerly located in Newark, N. J., has opened an office and laboratory at 239 Waverly Avenue, Brooklyn, N. Y.

SECTION NEWS

New York Metropolitan Section

The last meeting of the season, held on May 14th, was Ladies' Night and a large turnout of members and their ladies enjoyed an evening of sociability as well as an excellent presentation of the subject of soaps and synthetic detergents. This was given by a well-known expert in this field, Dr. Cornelius T. Snell. The many questions from the floor were sufficient evidence that Dr. Snell had held the attention of her audience.

Favors of flowers and door prizes for the ladies added to the festive nature of the occasion.

At a short business meeting preceding the program, the following officers were elected for the coming year.

Chairman—A. C. Loonam
Vice-Chairman—Herbert Bandes
Secretary-Treasurer—F. A. Lowenheim
Executive Committee—J. S. Mackay, *ex officio*, M. B. Diggin, M. F. Quaely, C. V. King.

F. A. LOWENHEIM, *Secretary-Treasurer*

San Francisco Section

The guest speaker at the March 19th meeting of the San Francisco Section was Donald K. Lippincott of the law firm of Lippincott and Smith, San Francisco. The subject of his talk was "Television."

Mr. Lippincott introduced his topic by discussing the developments leading to television as we know it today—from its very beginnings back in 1837 when Morse made his initial inventions. Mr. Lippincott's remarks throughout this part of his talk were made especially interesting because of the very close contact he has maintained with Charles Farnsworth who has probably made as great a contribution to the development of television as any other single person. Personal anecdotes of the speaker's experiences during some of the legal proceedings connected with television inventions were also most entertaining.

Mr. Lippincott devoted the latter part of his talk to a discussion of the setting up of standards by the FCC and radio and television manufacturers —and how they will affect the future. He also discussed color television in its present stage of development and its probable effects on the future of the industry.

The speech was delivered in a highly interesting manner and was thoroughly enjoyed by all who attended.

R. F. BECHTOLD, *Secretary-Treasurer*

NEW MEMBERS

In May 1952, the following were elected to membership in The Electrochemical Society:

Active Members

JOSEPH D. AJZENSTADT, Ran Ltd., P.O. Box 648, Tel-Aviv, Israel (Battery)

WILLIAM N. CARSON, JR., General Electric Company, mailing add: 1308 Putnam, Richland, Washington

ANTHONY R. CIUFFREDA, Standard Oil Development Company, mailing add: 75 West Hill Rd., Colonia, N. J. (Corrosion)

CHARLES H. CLAPHAM, JR., Tele-Ray Tube Company, mailing add: 19 Saranac St., Dobbs Ferry, N. Y. (Electronics)

PRESCOTT R. DICKINSON, General Electric Company, Chemical Products Works, 1099 Ivanhoe Rd., Cleveland, Ohio (Electronics)

PHILIP H. DOWLING, Philips Laboratories, Inc., mailing add: 22 Midchester Ave., White Plains, N. Y. (Electronics)

ARTHUR C. HASKELL, JR., National Lead Company, mailing add: 420 Southwood Dr., Kenmore, N. Y. (Electrothermic)

RAY C. HUGHES, Philips Laboratories, Inc., Irvington-on-Hudson, N. Y. (Electronics)

ALOIS J. KALLFELZ, Allied Chemical & Dye Corporation, mailing add: 509 Summit Ave., Syracuse, N. Y. (Industrial Electrolytic)

ROLAND P. KOEHRING, Moraine Products Division, General Motors Corp., 1420 Wisconsin Blvd., Dayton, Ohio (Corrosion, Electrodeposition, Electrothermic and Theoretical Electrochemistry)

EDWARD L. LIND, Radio Corporation of America, Princeton, N. J. (Electronics)

J. W. LOVELAND, Sun Oil Company, Research Laboratory, Norwood, Pa. (Electronics)

MELVIN L. MANNING, Pennsylvania Transformer Company, Canonsburg, Pa. (Electric Insulation)

VINCENT P. MCCONNELL, General Electric Company, mailing add: 269 Whittier Ave., Syracuse, N. Y. (Corrosion and Electrodeposition)

CHARLES F. MILLER, 105 Maryland Hall, The Johns Hopkins University, Baltimore, Md. (Electric Insulation and Theoretical Electrochemistry)

ROBERT A. OLER, Solvay Process Division, Allied Chemical & Dye Corporation, mailing add: 1150 Bellevue Ave., Syracuse, N. Y. (Industrial Electrolytic)

K. S. RAJAGOPALAN, Technical Development Establishment Laboratory Stores, Kanpur, India (Electrodeposition and Theoretical Electrochemistry)

W. E. RUTHER, Argonne National Laboratory, mailing add: 3827 Harvard, Skokie, Ill. (Theoretical Electrochemistry)

W. W. SELLERS, JR., International Nickel Company, mailing add: 153–10 61st Rd., Flushing, L. I., N. Y. (Electrodeposition)

RUSSELL B. SNYDER, % Rauland Corporation, mailing add: 4245 N. Knox Ave., Chicago, Ill. (Electronics)

JOHN C. STAHL, U. S. Bureau of Mines, mailing add: Box 82, Rolla, Mo. (Electrodeposition and Theoretical Electrochemistry)

MARTIN E. STRAUMANIS, School of Mines and Metallurgy, Department of Metallurgy, Rolla, Mo. (Corrosion and Theoretical Electrochemistry)

KENNETH M. TAYLOR, Carborundum Company, mailing add: 1045 River Rd., Lewiston, N. Y. (Electronics)

ROBERT C. TURNER, Division of Chemistry, Science Service Bldg., Ottawa, Ontario, Canada (Theoretical Electrochemistry)

RODGER D. VENEKLASEN, National Research Corporation, 70 Memorial Dr., Cambridge Mass. (Electronics, Electrothermics, and Industrial Electrolytic)

V. A. WENTE, Naval Research Laboratory, mailing add: 2715 30th St. S. E., Washington, D. C. (Electric Insulation)

CHARLES R. WILKE, College of Chemistry, University of California, Berkeley, Calif. (Battery, Industrial Electrolytic, and Theoretical Electrochemistry)

Reinstatement

WILLIAM C. ARSEM, Office of Naval Research, mailing add: 5520 Glenwood Rd., Bethesda, Md. (Battery, Industrial Electrolytic, and Theoretical Electrochemistry)

Associate Members

WILLIAM W. FAIRCHOK, The Cleveland Electric Illuminating Company, mailing add: 1840 E. 97th St., Cleveland, Ohio (Electrothermic and Industrial Electrolytic)

DAVID E. KINNEY, General Electric Company, mailing add: 2346 Euclid Heights Blvd., Cleveland, Ohio (Electronics)

ALAN L. MCCLELLAND, Department of Chemistry, University of Connecticut, Storrs, Conn. (Theoretical Electrochemistry)

WILLIAM H. REDANZ, Columbia University, mailing add: 421 E. 72 St., New York, N. Y. (Theoretical Electrochemistry)

Student Associate Members

CHIEN-YEN CHENG, University of Michigan, mailing add: 524 Packard St., Ann Arbor, Mich. (Industrial Electrolytic and Theoretical Electrochemistry)

JOHN D. MOVIUS, Stevens Institute of Technology, mailing add: 812 Castle Point Terr., Hoboken, N. J. (Corrosion)

Correction

In the paper by S. Pakswer and P. Intiso entitled "Liquid Settled Luminescent Screens" published in the April issue of the JOURNAL, p. 164, the Greek letter "Xi" was used in place of "Zeta" in referring to the "Zeta potential."

LETTER TO THE EDITOR

Influence of Electrolyte *p*H on emf of LeClanche Cells

Dear Sir:

Previous work[1] has shown that the emf of Leclanché cells is influenced by the *p*H of the electrolyte which is in direct contact with the MnO_2 particles. In dry cells this part of the electrolyte, which is contained in the pores of the bobbins and which will be called hereinafter "the catholyte," is responsible for part of the emf drop during shelf life and during discharge of the cells.

To prove this, cells were subjected to (A) a heavy continuous discharge, whereby the catholyte *p*H is increased steadily by the NH_4^+ in the bobbin, and (B) a light intermittent discharge. Catholyte *p*H and emf remain constant after some time.

Test procedure.—Uniformly prepared dry cells (size "B") were discharged through 5 ohms per cell. Some of the cells were opened at various states of discharge, their bobbins ground and extracted with 50 ml water each. This amounts to a dilution of the original quantity of catholyte of about 40-fold. The *p*H was measured in the extract after filtration.

In test A the emf of the unused cells was 1.63 v and the *p*H of the (40-times diluted) catholyte was 4.8. The closed circuit voltage (ccv) through 5 ohms, of 1.53 v, dropped after 4 hours' discharge time to 0.80 v. Then the circuit was opened. After one hour rest the emf had risen to 1.05 v, the *p*H of the (40-times diluted) catholyte was 8.0. After 36 hours' rest the emf increased to 1.20 v. Now, the ccv was 0.86 v and dropped in the following 3.5 hours to 0.55 v. The total discharge time was 4 + 3.5 = 7.5 hours. Two hours after the circuit was opened the emf was 0.76 v, the catholyte *p*H 9.4. Table I shows the results.

In test B an intermittent discharge through 5 ohms, 10 min per day, gave the results listed in Table II.

TABLE I. *Test A, continuous discharge 5 ohms, cells B*

Cells	emf	*p*H catholyte (40 × diluted)
Unused cells	1.63 v	4.8
After 4 hours discharge	1.05 v	8.0
After 7.5 hours discharge	0.76 v	9.4

TABLE II. *Test B, intermittent discharge, 5 ohms, 10 min per day*

Cells	emf v	*p*H catholyte (40 ×diluted)	ccv v
Unused cells	1.63	4.8	1.53
After 3 days (30 min)	1.57	6.4	1.43
After 10 days (100 min)	1.46	7.1	1.30
After 28 days (280 min)	1.30	7.3	0.82
After 54 days (540 min)	1.30	7.3	0.72

It is to be understood that the figures given above do not allow a calculation of a fixed ratio, Δ emf : ΔpH, for the following three reasons:

1. There are still other reactions in a dry cell influencing the emf of the bobbin next to the catholyte *p*H.

2. The *p*H measured and noted above was obtained in solutions containing the catholyte 40-times diluted with water. A calculation of the true *p*H value of the (very thin) electrolyte layer in direct contact with the surfaces of the MnO_2 particles is not advisable, as it is experimentally impossible to separate this very thin electrolyte layer from the electrolyte contained in the comparatively large spaces of the bobbin pores.

3. The emf of the whole galvanic cell was measured. To calculate the emf: *p*H ratio, the influence of the acidification of the anolyte during discharge should be measured as well and its influence on the cell emf taken into consideration. With this reservation, there is no doubt that the emf of Leclanché cells is influenced by the *p*H of the catholyte.

C. DROTSCHMANN
Utrecht, The Netherlands

[1] C. DROTSCHMANN, *Metall*, 1948, 37–41

BOOK REVIEWS

CORROSION, CAUSES AND PREVENTION, 3rd ed., by Frank N. Speller. Published by McGraw Hill Book Company, New York, 1951. 686 pages, $10.00.

In 1926, when the first edition of this book was completed, corrosion control was in the working vocabulary of not more than a handful of engineers. The subject up to that time made but small impress on either industries or universities, and the corrosion engineer was still in the distant future. But the picture changed rapidly, and technical contributions both from this country and abroad opened up a new field of knowledge that proved to be of major concern to all industries, and to a world population faced with shrinking metal supplies and an urgent need to conserve human and material resources.

"Corrosion, Causes and Prevention" provided the first systematic guide to the diverse trails, traverses, footholds, and other climbing techniques in the new field of corrosion engineering. Many are the individuals and groups who avoided getting their toes stubbed or missing the trail by reference to this early Baedeker. Frank Speller, in the present 3rd edition of what might be termed his introduction to corrosion engineering, is now able to write, "The fact that millions are now being profitably spent every year under the supervision of hundreds of skilled corrosion engineers to mitigate such losses indicates that corrosion is now recognized as a major problem." It must be with considerable satisfaction that this statement is made by one who devoted a lifetime to mitigating corrosion, and who as "Dean of Corrosion Engineers" witnesses today the growing maturity of a subject he nurtured and encouraged so patiently.

The 3rd edition, like those that preceded it, contains a wealth of information on factors affecting corrosion of iron and steel, and is concerned almost entirely with ferrous metals. The current pertinent data on this subject obtained by many investigators, and scattered over a broad cross section of the technical literature, have been conveniently assembled and summarized in this volume. The second chapter on theory has been supplemented and extended. The third and fourth chapters on "Influence of Methods of Manufacture and Treatment" and "Factors Internal to the Metal," continue to be classical treatments of these subjects. They reflect the intimate knowledge gained by the author through his close association with the steel works over many years. There is no book that handles this phase of the matter as thoroughly, nor as authoritatively. It is in this section that Dr. Speller gives advice to the younger generation well worth heeding. "To obtain a high grade uniform product," he states, "as well as quantity production, it is of great advantage for one organization to have complete control of all operations from the mining of the ore to the finished product." And again, "It should be understood that, for many purposes, a high standard of quality is more important than large tonnage records."

A discussion is included for the first time on the influence of micro-organisms on corrosion—further proof of the complexity of corrosion and its broad ramifications. Also, a chapter has been added on cathodic protection, the field of activity which did more than any other to initiate the corrosion engineer, and which proved how valuable he could be to industry. Discussion of corrosion fatigue has been augmented, and there is brief mention of stress corrosion cracking and fretting corrosion, all subjects of great importance to the mechanical and chemical engineer but about which so little is known. These gaps in a rapidly growing subject must someday be filled in by present and future corrosion investigators. The Appendix has been expanded and contains much useful information such as general conversion factors, glossary of terms used in corrosion, and a treatment on factors in metal selection.

In the last chapter we read, "... much has been accomplished to reduce the ravages of corrosion, and it may now be said that there are very few situations where some economical remedy cannot be applied by changing the environment, by isolating the metal from destructive environment, or by building up corrosion resistance of the metal." And finally, "... as in research that affects public health, ... more work should be done on the study of the fundamentals in order that corrosion prevention may be put on a sound scientific basis." Dr. Speller has contributed personally to the accumulation of such basic knowledge and, in addition, by completing the 3rd edition of his useful book has provided another rung to the ladder by which others may climb up and view the world of science and technology beyond the present horizons.

H. H. Uhlig

Fluid Flow in Pipes by Clifford H. McClain. Published by The Industrial Press, New York. 123 pages, $3.00.

The first chapter of this book is entitled "Dimensions of Fluid Properties," and discusses weight, specific gravity, the ideal gas law, velocity head, etc. The second chapter, on "Viscosity of Fluids," derives Poiseuille's law, and the equation for rotational viscometers (neglecting, however, the variation in radius). It also gives the average empirical equations for the commercial capillary efflux viscometers. In a derivation of the Saybolt equation, however, two mistakes are made—the capillary length is subtracted from total head, and the arithmetic mean instead of the logarithmic mean head is employed. The Walther and Sutherland equations for effect of temperature on viscosity are also given. The chapter on "Effect of Piping on Fluid Flow" discusses Reynold's Number and gives the Moody friction factor and roughness charts. The fourth chapter on "Design Practice" applies Bernoulli's principle to several cases and gives discharge coefficients for orifices and fittings, etc.

This book is nicely printed on thick paper, clearly written, and adequately illustrated. It evidently can serve as a text in the minimum essentials of fluid flow for one with no previous contact with the theory of the subject.

Charles F. Bonilla

Gmelins Handbuch der Anorganischen Chemie. System No. 41 Titan. Gmelin Institute, Clausthal-Zellerfeld. Published by Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1952. Available in the U. S. from Walter J. Johnson, Inc., and Stechert-Hafner, Inc., New York. 481 pages, DM 113.

After Du Mont's titanium bibliography and after Barksdale's titanium monograph, Gmelin's Titan rounds up our field of knowledge of this element. It would hardly be possible to cram more information in the 481 pages of this book, which is written with Gmelin's traditional care and thoroughness. Thanks to the assistance given by the American Chemical Society, the literature references of the United States have been fully recorded up to the end of December 1949. The title pages mention twenty-five collaborators of the volume by name. It appears that this colossal work is the most important contribution to the chemistry of titanium of the present time, not only because of the completeness of its bibliographical data, but also because of its cautious scanning of the material presented.

The first 78 pages concern the occurence of titanium, the kind of minerals in which it is found, their way of formation, and their physical and chemical properties. The next 38 pages cover the production of titanium oxide, including pigment. The revolutionary new process for producing pigment without using any sulfur, which is based on the combustion of titanium tetrachloride with oxygen or oxidizing gases, is described on one-third of a page, yet more than two dozen references are brought out. Ore dressing, breaking up of the minerals with acids or alkalies, hydrolysis of sulfate solutions, production of seed solutions, purification of the precipitate and its calcination are exhaustively given. So numerous are the references in some places that they represent well over fifty per cent of the text.

The 11 pages following the above concern the production of the metal. It would appear impossible to condense so much material on so few pages if it was not cut down to the essentials, yet the reduction of TiO_2 with C, CO, H_2, CaC_2, CaH_2, Ca, Mg, Na, Si, Al and that of $TiCl_4$ with Si, H_2, Na, Ca, Mg is well covered. The reduction of double fluorides and of various halides

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by other elements or by fusion electrolysis is stressed, and the dissociation of the iodide is described fairly completely. Four pages are devoted to the production of the pure metal and to that of its various forms such as powder or coatings.

The physical properties comprising atom structure, crystallographic, mechanical, thermal, optical, magnetic, and electrical characteristics are discussed on 54 pages. The electrochemical behavior is shown on 3 pages, the chemical activity on 9. This comprises corrosion, alloy formation, production of oxides, sulfides, carbides, nitrides, and halogenides. The alloys, namely those with Be, Zn, Cd, Hg, Ga, In, and La, are treated on two pages only. The system titanium-hydrogen covers 7 pages, the oxides take 60, in which production methods, physical and chemical properties are duly considered. Fifteen pages take care of the system titanium-nitrogen. The fluorides are treated on 2 pages, the chlorides on 35, the bromides on 7, and the iodides on 5. The sulfides are spread over 15 pages.

The next chapters concern the compounds, intermetallic and others, of titanium with Se, Te, B, C, Si, P, As, Sb, Li, Na, K, NH_4, Rb, Cs, Be, Ca, Sr, Zn, Cd, Hg, Th, and rare earths. It would be beyond the scope of the present review even to try to give an idea about the vastness of the information offered here, but it may suffice to mention as an example that the physical properties of titanates, comprising the complicated dielectric phenomena, are reviewed in a number of sections with exhaustive bibliographical data. The rest of the book treats the chemical reactions of various titanium salts.

A publication such as this can of course not be read as a whole; it can only be used page-wise for its references. It forces even the expert to modesty and should be the best source of data for inventors and for their counterparts, the patent examiners. A careful look shows, however, how little we really know positively about the element titanium, despite the fact that a book of so many pages could be written about this subject. Great progress in techniques is usually brought about by pioneers with little knowledge, who do not wait for the men in the ivory towers to catch up with basic data. Our present search for cheaper titanium production methods is severely handicapped by this lack of basic knowledge. Would it not be advisable to spend some of the millions, wasted today in ignorance, to underwirte basic titanium research in universities and in similar institutions? The new Gmelin, despite the fact that our knowledge of titanium chemistry is still so sketchy, will be found on the book shelves of everybody engaged in the titanium field. The need for a good translation is evident.

W. J. KROLL

TEXTBOOK OF ELECTROCHEMISTRY, Volume II, by G. Kortüm and J. O'M. Bockris. Published by Elsevier Press, Inc., Houston, Texas, 1951. xiii plus 530 pages, $10.00.

Volume I of this Textbook was reviewed in the JOURNAL, in February, 1952, page 43C. The two volumes have continuous numbering of page and chapter, and a single index at the end of Vol. II; it would have been helpful and not impossible to have put the book in one cover.

Chapter X deals with interfaces—electrocapillary phenomena, double layer theory, electrophoresis, and related topics. Chapter XI treats irreversible electrode processes; overpotential and those processes (isotope separation, deposition, oxidation, reduction, dissolution) which are dependent on or greatly influenced by overpotential; passivity, electrochemical corrosion, electrolysis of high temperature melts. There is an interesting section on fuel cells. To achieve brevity, unfortunately only a few electrolytic reactions are discussed. A wrong impression of the Kolbe synthesis is given since many higher fatty acids actually do yield alkanes.

Chapter XII is on electrical processes in gases, with sections on the mechanism of conduction and the nature of discharges, and on chemical reactions caused or influenced by electrical discharge. This chapter has not been as thoroughly modernized as most of the book has.

Chapter XIII, written by Roger Parsons, attempts to give some idea of the many experimental methods available for electrochemical work. Since in 85 pages all descriptions must be brief if an adequate variety of methods even receive mention, the author supplements his presentation with some 330 literature references. Many readers will wish that certain topics, such as electroanalytical methods, could have been covered more thoroughly.

Chapter XIV consists of 160 pages of numerical data, tabulated by B. E. Conway. These include universal constants, physical properties (ionic e tropy, radii, polarizability, dielectr constants), osmotic and activity coef cients, conductance, transference num bers, diffusion coefficients, *p*H of bu fers; and standard electrode potentials The accuracy or precision of the dat is evaluated so far as possible and som 760 references to sources are given These tables will be enormously useful but it is to be deplored that author find it necessary to incorporate such tables in books of this type. Modern "International Critical Tables," with really complete coverage of data, are badly needed.

One hundred and twenty example and problems complete the book These range from simple numerica problems to rather difficult derivation and extended computations. Answers are given as well as methods of working the more difficult examples.

This volume has fewer proofreader errors than Vol. I. To mention a few Hickling is misspelled MacKling (p 583); Droz is misspelled Drosz (p 580); on p. 803 the exponents of K_1 K_2 are reversed. One wonders if th numerical data in Chapter XIV have been carefully checked.

The book is highly recommended fo just those it was primarily intended to serve: students who need a good back ground in physical chemistry with emphasis on the electrochemical as pects. It will be useful to others who wish to modernize their background o find quick reference to some topic.

CECIL V. KIN

CORROSION GUIDE by Eric Rabal Published by Elsevier Press, Inc Houston, Texas, 1951. 629 page $12.50.

This book is essentially a compilati of tables listing the chemical resistan of about 40 materials of construct with respect to about 250 corrosi substances, the latter arranged alph betically. The tables are similar those of the German Dechema, t summarize current experience on ma terials of construction in the chemic industry.

Materials of construction are clas fied as: *Practically resistant*, *fair resistant*, *not resistant but used in pra tice*, and *unusable*. The corrosion rat when given, are in the units of mil meters per year or grams per squa meter per day, which is 1/10th the u used in this country, namely, milligra per square decimeter per day (mdd

The mechanics of publishing the tables has unfortunately left many partly blank pages which add to the cost and size of the book.

The volume is introduced by a general discussion of corrosion and corrosion test methods. The author takes an unnecessarily dim view of potential measurements, perhaps because he expects strict parallelism with corrosion rates. Even though this parallelism does not exist generally, it is unfortunate to have the reader remain with the impression that measurements of this kind are not useful. In cathodic protection alone, measurements of potentials are important.

A few errors of statement occur. On page 20, it is said that iron corrodes only slightly in distilled water because the conductivity is low. Actually, the corrosion rate is often higher in distilled water than in natural waters where the conductivities are considerably greater. On page 23, it is said that carbon dioxide from the atmosphere usually accentuates corrosion, although W. H. Walker in 1907, and Whitman and Russell in 1923, showed that carbon dioxide of the atmosphere was not especially significant with regard to the corrosion rate of iron exposed to the atmosphere or totally immersed. Figure 14 mentions "austenite steel," whereas probably austenitic 18 8 stainless steel is meant. At the bottom of page 41, 18-8 stainless steel is said to be sensitized to intercrystalline corrosion by "longer heating to 600° and slow cooling," whereas what is probably intended is "heating at 600°C, or slow cooling through 350°–800°C sensitizes 18-8."

Some misunderstanding may occur through what appears to be terms translated from the German. On page 10, for example, it is said that the potential is "refined" owing to amalgamation. Similarly, iron is said to enter solution in the "hydratised" form. On page 21, potassium ferricyanide becomes "ferric potassium cyanide." "Blank" test has been translated "blind" test on page 37. There are other instances of the same kind.

The tables contain a great deal of useful practical information, some of which has apparently not been published before. The book should be helpful to the chemical engineer, who has some experience with materials of construction, and who is concerned with the construction of new equipment, or who is anxious to compare his present practice with that representative of a broad cross section of the chemical industry. It will probably not be as useful to the engineer who through lack of experience is unable to exercise some judgment in applying the information.

H. H. Uhlig

The Welding of Non-Ferrous Metals by E. G. West. Published by John Wiley & Sons, Inc., New York, 1951. × plus 553 pages, $8.50.

This is a good general text on the welding of nonferrous alloys. The book is essentially designed to aid all those who actually wish to weld in practice. The metallurgy presented appears sound. Relatively large sections of the book are devoted to timely information pertaining to the welding of aluminum, magnesium, and their alloys. Very little material is presented on automatic processes. The illustrations and charts are numerous and excellent.

E. E. Schumacher

RECENT PATENTS

Selected for electrochemists by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

February 26, 1952

Högel, L., and Jaekel, J., 2,587,045, Clamping Device for Electrodes of Arc Furnaces

Victoreen, J. A., 2,587,254, Indicating Pocket Ionization Chamber

Seaver, J. D., 2,587,391, Thermocouple

March 4, 1952

Butler, K. H., 2,587,592, Barium Mesotrisilicate Phosphor

Konrad, E. H., and Eustis, W. E. C., 2,587,630, Method for Electrodeposition of Iron in the Form of Continuous Strips

Rojas, F. A., 2,587,651, Method and Means for the Electrodeposition of Chromium

Horswell, A. H., and Horswell, A. H., Jr., 2,587,727, Tiltable Induction Furnace

Jones, D. E., and Ryde, J. W., 2,588,008, Germanium Crystal Rectifiers and Method of Producing the Crystal Element Thereof

Perkins, M. A., and Couper, M., 2,588,041, Separation of Metal Values in Fluoride Compositions

Smith, W. A., 2,588,170, Secondary Battery

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Mr. J. K. Knight, Engineering Department
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Lark-Horovitz, K., and Whaley, R. M., 2,588,253, Alloys and Rectifiers Made Thereof

Lark-Horovitz, K., Benzer, S., and Davis, R. E., 2,588,254, Photoelectric and Thermoelectric Device Utilizing Semiconducting Material

March 11, 1952

Watkins, F. M., 2,588,441, Prevention of Corrosion

Zadra, J. B., 2,588,450, Process of Regenerating Activated Carbon Loaded with Adsorbed Gold

Findley, H. J., 2,588,508, Thermoelectric Generator

Peaslee, R. L., 2,588,566, Electrolytic Process for Stripping Copper

Gochenour, R. B., and Gochenour, A. M., 2,588,716, Process and Apparatus for the Irradiation of Liquids

Kolodney, M., 2,588,734, Pretreatment of Beryllium Prior to Coating

Tanner, G. S., 2,588,776, Apparatus for Testing Storage Batteries

Cubitt, R. H., and Sell, R. G., 2,588,806, Alternating Current Rectifier of the Dry Surface Contact Type

Davis, J. V., 2,588,910, Anode Shifting Device

Carlson, T., 2,588,962, Flashlight and Hearing Aid Battery Booster

Troy, W. C., 2,588,998, Thermocouple

Galasso, A. A., 2,589,071, Battery Holder

Olson, A., 2,589,122, Battery Terminal Connector

Weinrich, A. R., 2,589,175, Aluminum Base Alloy for Metal Evaporation

March 18, 1952

Smith, A. D., 2,589,301, Electric Melting Furnace

Smith, A. L. J., 2,589,513, Method of Making Titanium Activated Calcium Magnesium Silicate Phosphor

Smith, G. B. L., and Leeds, M. W., 2,589,635, Electrochemical Process

Dickover, M. W., 2,589,681, Battery Plate

Governale, L. J., Huguet, J. H., and Neher, C. M., 2,589,689, Photochemical Chlorination Process

Wood, W. S., and Clennett, G., and Hulland, H. L. 2,589,982, Electrolytic Production of Ammonium Persulfate Solutions

March 25, 1952

Wilke, M. E., 2,590,284, Electric Terminal for Dry Batteries

Janser, A. M. J., and Townsend, C. S., 2,590,323, Electrical Apparatus

Isenberg, S., 2,590,411, Cerium Activated Aluminate Phosphors Active in the Erythemal Range

Loverde, A., 2,590,426, Process for Photochemical Chlorination of Hydrocarbons

Taylor, R. L., 2,590,584, Sea-Water Battery

Miescher, K., Ehmann, L., and Wettstein, A., 2,590,637, Direct Halogenation of Steroids with an Unsaturated Side Chain in 17-Position and the Dehydrohalogenation of Resultant Products

Rosenberg, D. S., 2,590,651, After-Chlorination of Polyvinyl Chloride

Homan, J., 2,590,703, Storage Battery Plate and Method of Forming Same

Vitale, A. S., 2,590,804, Battery Casing

Roehrl, B. C., 2,590,824, Battery

April 1, 1952

Brandt, W. H., Rider, M. W., and Westphal, R. C., 2,590,927, Electrolytic Method of Removing Burrs

Gray, R., 2,590,960, Electrolyte Level Indicator and Antisplash Device for Electric Accumulators

Berman, H. and Prupis, R. I., 2,591,042, Apparatus for Electrolytic Treatment of Spaced Metallic Elements

Héraud, A., 2,591,355, Electric Battery Composed of Flat Elements

Ward, H. K., 2,591,479, Method of and Solution for Coating Surfaces Chiefly of Zinc

Fox, A. L., 2,591,532, Depolarizer for Primary Cells

April 8, 1952

Lubatti, E., 2,591,708, Electric Glass Furnace

Lubatti, E., 2,591,709, Furnace Electrode

Wilson, H. D., and Quick, J. H., 2,591-754, Battery Separator

Wilson, H. D., and Popper, C., 2,591-755, Storage Battery Separator

Jones, T. C., and Jones, Anna C., executrix of said T. C. Jones, deceased, 2,591,826, Galvanic Water Correction Device

Carroll, C. C., 2,592,115, Neutron Source

Howell, W. N., and Hill, H., 2,592,144, Process for the Electrolytic Production of Fluorine

Stamper, W. Y., 2,592,207, Portable Battery

Fonda, G. R., 2,592,261, Halophosphate Phosphors

Lee, V. A., 2,592,439, Dry Cell Seal Closure

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Editorial

Primary Batteries 1902-1952

THE YEAR in which The Electrochemical Society was founded may be said to mark the end and beginning of two important eras in primary-battery history. During the first seventy-five years of the preceding century the primary battery was the only practical source of continuous electric current, thereafter yielding gradually to the Gramme dynamo. As the high-power primary-battery era was drawing to a close about 1902, the present era of ever-smaller portable primary cells and batteries was starting, with the Leclanché-type flashlight-size dry cell just beginning to be marketed. Other cell systems have been developed and marketed since then but the dry cell continues to dominate the primary-battery market with sales of about 100 million dollars in 1951.

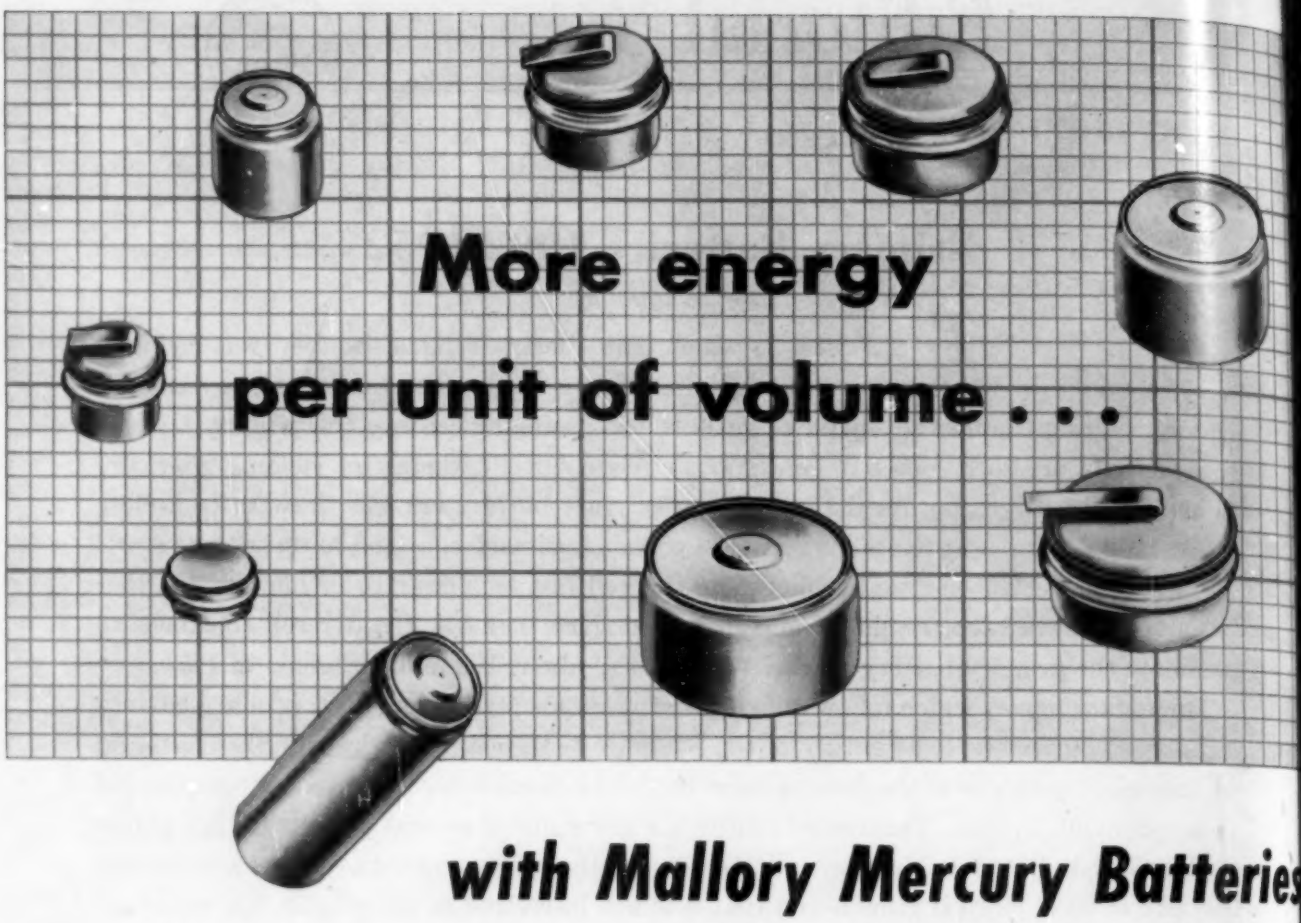
The review papers which follow record the remarkable progress made in primary-battery technology during the half-century of the Society's existence. They describe the continual technological progress in the development of the Leclanché dry cell—a very complicated thermodynamic system. This record refutes the criticisms of several persons in high places to the effect that the dry-battery industry during these fifty years has shown a relatively low rate of technological growth and that it is not interested in using basic raw materials other than those originally used. The record amply justifies the continued use of these raw materials although large sums of money have been spent during the past decade, particularly by the government, in an endeavor to replace these time-honored materials and constructions. The Leclanché cell still is pre-eminent.

The dry-battery industry has weathered the combination of normal business depressions and technologically imposed depressions, particularly when storage batteries replaced dry batteries in automobiles and alternating-current-powered radio receivers replaced those powered by dry batteries. Each time *smaller* and *better* batteries were important factors in overcoming these recurring depressions.

The review papers show that the primary-battery industry has developed and manufactured, in addition to the Leclanché cell, a variety of cell systems, both for civilian and military use. Some were based on previously unused cell systems. The older types were revised and improved to meet successfully the new and unusual military conditions of use.

The primary battery also has continued to be of important social significance apart from the prominent part it plays in instruments of destruction. Radio communication, to which the primary battery contributed, has changed greatly our social habits and the nature of our government. The interest of people in war, in the world series, or in an election is reflected in battery sales. Most households and cars contain one or more flashlights. In less-electrified areas of the world, the flashlight is of great value as is evidenced by the exportation of over 100 million flashlight cells in 1951. And of particular importance are the pocket hearing-aids powered by miniature batteries which have restored hearing to many thousands of persons.

The primary-battery industry looks with confidence to the future! —O. W. STOREY



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Fiftieth Anniversary

THE ANNIVERSARY ISSUE ON PRIMARY CELL SYSTEMS

Foreword

The following review papers cover most of the primary ll systems which either are being produced commercially have been engineered and tested so that they are ready commercial production.

Each paper presents a concise review of the cell system volved and, as a rule, covers history, theory of operation, nstruction, operating characteristics, production data, and lds of application. Of particular interest is that operating ta are presented in such form that direct comparisons can made between different systems. Output data are pre- nted as functions of unit volumes and weights of the cells d are supplemented with data for current density per unit ea of active electrode surface.

Although the review articles were prepared by the authors hose names are indicated, each review represents the com- site knowledge, experience, and judgment of many other ualified members of the Battery Division. It is appropriate at we acknowledge, formally and with sincerity, that the following men have given much of their time to make this Anniversary Issue so complete and so authoritative:

O. W. Storey	C. C. Birdsall
N. C. Cahoon	U. B. Thomas
P. L. Howard	J. C. White
W. S. Herbert	R. C. Kirk
C. K. Morehouse	G. B. Ellis
J. M. Booe	G. W. Heise
N. Hackerman	E. A. Schumacher
W. C. Vosburgh	P. S. Brooks
J. J. Coleman	J. Musgrave

The Chairman of the Battery Division hereby expresses his personal appreciation of the work of these men and the authors.

He also wishes to express, as spokesman for the entire Battery Division, appreciation to The Electrochemical Society and its Officers and Editorial Staff for publication of this comprehensive review issue.

—J. N. Mrgudich

Dry Cells of the Leclanché Type, 1902-1952—A Review

George W. Heise[1] *and N. C. Cahoon*[1]

Although the early development of the dry cell in the nited States proceeded as an art rather than a science and chnological progress was slow,[2] the advances made during e past 50 years have been spectacular. At the turn of the entury, to be sure, the cell had already been converted om the original wet element (2) into a portable dry unit, nd the plaster of Paris separating anode and cathode in e Gassner cell (3) had given way to cereal paste or paper ner.[3] In contrast with the 20,000 wet batteries in use "in rance and abroad" triumphantly claimed by Leclanché in 868, production of dry cells had reached the dizzy height, the United States alone, of two million units per year, ostly of the conventional six-inch size. The flashlight (5) ad been introduced (6) and was beginning to achieve some ommercial importance, yet it would have taken a crystal all of unusual clarity to enable anyone at that time to fore- ee the enormous present usage of this and other miniature ell types[4] (over two billion annually in the United States alone). Further, there was little reason to predict the parallel rise in cell quality, which increased the useful service of the six-inch dry cell from perhaps 8 to 10 ampere hours to its present level of 55 or 60, and which has more than doubled the capacity of the flashlight battery in the last 15 to 20 years (7). This improvement has been of particular interest to the technologist because it was achieved without any essential change in cell constituents.

The task of singling out the factors which have contributed in greatest measure to the evolution of the modern dry cell is not an easy one; it is even more difficult to assess their relative merits. Sometimes items long known in the battery art failed to find application in dry cell technology for many years; frequently a simple mechanical improvement has had greater immediate impact on battery quality than, for example, a basic contribution to our knowledge of cell reactions. Amalgamation goes back to the very beginnings of the primary battery (8) and was actually used by Leclanché; yet this method of reducing wasteful zinc corrosion and improving keeping quality in the dry cell, though practiced to some extent, was not generally adopted until about 1910. The so-called bag-type cell, in which the molded depolarizing mix "bobbin" was wrapped with cloth[5] and a paste or gel electrolyte was used, appeared at an early date (10). In the U. S., at least, a paper or pulpboard liner (11) largely supplanted cereal paste in the six-inch cell, no doubt facilitating manufacture by making it possible to ram or pack the depolarizing mix into the cell container, but hardly calculated to increase service capacity or to improve shelf maintenance. The application of a cereal paste to the paper or pulpboard liner, a

[1] National Carbon Research Laboratories, Cleveland, Ohio.

[2] "One is at a loss," said Professor Crocker in 1906 (1), "to oint out any radical or even important advance in primary atteries . . .; the types now on the market . . . are not subtantially better than what might have been obtained 60 years go."

[3] Portable cells with immobilized (gelatinous) electrolyte, g., the Guerin (agar) and the Leclanché-Barbier modifica- ions described by Tomassi (4), seem to have anticipated the assner type by some years, although the latter may have een one of the first commercial cells in which the zinc anode erved as cell container.

[4] As late as 1908, Burgess fixed the two sizes of his first small ells "by the sawed-off ends of a broom-handle and a shovel- andle, respectively, around which the zinc cans were formed" Ref. (6), p. 174].

[5] The use of cloth as replacement for the porous pot of the original Leclanché element probably originated with the wet cell (9).

major improvement factor known at least as early as 1893 (12), was not generally practiced until about 1915. Paper itself passed through many stages of composition and thickness to the thin kraft (13) now standard in the large six-inch and many of the small flat-type cells.

Meanwhile, other variations in cell design appeared, particularly in the smaller sizes. The flashlight cell, in general, employed the bag-type construction, in which the separately molded mix bobbins were protected by wrappings of cloth or paper (14), or by coatings of paste itself (15). The development of mechanically stronger bobbins and changes in cell manufacturing methods largely eliminated the need for such wrappings (16) and they are no longer widely used. Much work was done on the gelatinization of cereal paste and to this day both the cooked and the cold-set (17) varieties have their proponents in the industry. A recent development which holds forth considerable promise is the plastic film (18), combining good contact with zinc and high ionic permeability, and capable of being used either separately or, like cereal paste, in conjunction with a supporting sheet.

The difficulty, encountered in miniature cells, of obtaining the high current densities required for flashlight service, further aggravated by a scarcity of suitable ores when World War I shut off the supply of Caucasian manganese, gave impetus to the development of precipitated or "artificial" MnO_2 depolarizers (19). These were usually expensive, and not altogether satisfactory, particularly with regard to their deleterious effect on keeping quality of cells. As new ore supplies, e.g., the Montana deposits, became available, and laboratories within the industry developed means for the better utilization of these, the artificial depolarizers for a time assumed a minor role in American technology and it is only in recent years that they have become of any great commercial importance.

Dramatic in its impact, although insufficiently recognized among battery technologists in general, was the work of Burgess (20) on "impalpable" graphite (particle diameter <10 microns) in battery mix which made possible the achievement, with natural ores, of flashlight service previously obtained only with artificial depolarizers. It was this work rather than the earlier suggestion by Burger (21) of the use of acetylene black that paved the way for the concepts of fineness, surface area, manganese:carbon ratios and mix conductivity on which much of our current technology depends. The process of milling both manganese dioxide and carbon together (22) produced a carbon of smaller particle size, and of greater surface area and covering power than could be obtained by separate milling. This made it possible to use the coarser, less expensive graphites as starting materials, and yet obtain mixes of improved conductivity, depolarizing activity, and absorptive capacity for electrolyte.

Acetylene black, made available in quantity chiefly through the effort of Shawinigan Chemicals Ltd., of Canada, came into commercial use about 1930 and has since largely replaced graphite as conducting carbon in the mix of the small cells.

The search for an artificial MnO_2, never, of course, completely abandoned, was intensified during the middle thirties when it became apparent that a depolarizer more active than the natural ore was needed to meet the increasing demands of the so-called industrial, heavy-duty flashlight service. The widespread use of an imported product was at least partly responsible for the development of new service levels, but only at the cost of serious lowering in shelf quality. Eventually American industry concentrated its efforts on electrolytic manganese dioxide (23), long considered a desirable depolarizer but not previously obtainable in form pure enough for many battery purposes because of contamination from the lead anodes used in its manufacture. The development within the industry of a suitably impregnated graphite electrode sufficiently resistant to anodic attack eliminated this difficulty. By 1940 (24) a satisfactory electrolytic manganese dioxide was in large-scale production and commercial use, and independence of foreign sources of artificial depolarizer had substantially been realized.

Recent years have been marked by some radical changes in battery construction. The first radio "B" batteries were simply groups of cylindrical cells connected in series. The need for space economy furnished the incentive for the development of flat cells which could be stacked, a construction very similar to that used in the original Volta pile (25). In the first commercially successful battery of this type (26) intercell connection was made by means of carbonaceous plastic coatings applied directly to the inert face of the zinc electrode. The perfection of thin coatings or separate conducting sheets and other refinements led to smaller and smaller batteries such as the "flat cell" (27) and various modifications of tray-type construction (28) so that now the demands of the portable radio receiver or hearing aid are met by miniature units which have no counterpart in the conventional round cell.

An important development in cylindrical cell construction as regards both the flashlight and six-inch units has been the introduction of metal or equivalent seals (29), better adapted to production methods, and much tighter than the pitch:rosin type of seal that they replaced. With these, both air access and moisture loss have been reduced, and the shelf quality of cell has been improved substantially.

At least one manufacturer has adopted a "metal-clad" construction (30) in which the entire unit, surrounded by an insulating jacket, is encased in a steel tube.

Worthy of mention, also, are the efforts made to use zinc not as cell container but as internal anode, completely surrounded by cathode mix (31). In the most recent of these (32) the zinc is in the form of centrally located vanes protected from the depolarizing mix by paper:film separators. A carbon:plastic lining on the cylindrical jacket serves as cathodic current collector or terminal. Potential advantages of this type of construction are greater electrode area, better utilization of zinc and, of course, freedom from leakage due to can perforation.

Most gratifying to the battery technologist are the advances made in our understanding of the cell reaction and the improvement in quality that has resulted from this knowledge. As long as the average user and, to some degree, even the manufacturer had no adequate means of evaluating product, there was no great incentive for intensive research, and technological progress was necessarily slow. The development of standards and tests, in which The Electrochemical Society initially took a leading part (33), has been carried on effectively by the National Bureau of Standards (34) and has done much to correct this condition. As the usage of the dry cell increased, bringing with it new and varied service requirements,[8a] the stage was set for fundamental studies as well as for product development and control; improvement

[8a] Performance curves for a general purpose "D" size flashlight cell and a "B" battery of flat type cells are shown in Fig. 1–4. For both cell types average values, rather than maximum service figures, are used.

n battery quality followed in due course. The enormous urrent demand for dry batteries for the widest possible range f storage and service conditions, for military as well as for ivilian applications, further stimulated work in this field nd, with the influx of Government and outside agencies, has rought the current volume of research to an unprecedented igh.

General Theory

Electrochemical theory, particularly as regards the development of electromotive force, was well advanced by 1900, yet the early battery technologists were slow to apply its teachings to the Leclanché system. Polarization was frequently considered loosely in terms of the cathodic liberation of hydrogen (35), though how the latter could be visualized as proceeding at the potential of the MnO_2 electrode or the operating voltage of the cell is not immediately clear. Depolarization, a term which we could well do without, is at best, as defined by LeBlanc (36), only a means of *preventing* evolution of hydrogen or oxygen; it has all too often been considered, not as the primary electrode process, but as a chemical reaction between MnO_2 and previously *liberated* hydrogen. There was little basis for this view (37), which regrettably is still found in many books on general chemistry and even in some electrochemical texts.

Much of the recent work on the over-all reaction in the dry cell has served to confirm previous findings rather than to blaze entirely new trails. Tomassi, in his text (4) on primary batteries issued in 1889, refers to earlier work in which various reaction products of the Leclanché wet cell were identified, among them the ammine $ZnCl_2 \cdot 2NH_3$ (38) and oxychlorides of the type $ZnCl_2 \cdot 3ZnO \cdot 4H_2O$ and $ZnCl_2 \cdot 6ZnO \cdot 10H_2O$. He wrote the equation for the over-all cell reaction essentially in its modern form:

$$Zn + Mn_2O_4 + 2NH_4Cl = ZnCl_2 \cdot 2NH_3 + Mn_2O_4H_2 \text{ (i.e., } Mn_2O_3 \cdot H_2O) \quad (I)$$

and cited conditions under which $Mn_3O_4 \cdot Zn$ (hetaerolite?) might be the reaction product.

For a long time, unfortunately, the equation for the cell reaction was of little help to the battery technologist. Actual service capacity, for example, might exceed by as much as 50 per cent that calculated from the NH_4Cl content, and even the reduction of MnO_2, because of air depolarization and other factors, could not immediately be correlated with cell behavior. In establishing cell formulations, empirical trial was necessary to obtain optimum compositions, and even these usually proved valid only for a limited set of service conditions. Definite progress was made when the various reactions which may occur during cell discharge were differentiated and identified, and some of the conditions determining their occurrence were established. Thus it is now recognized (39) that in an electrolyte containing more than 8 to 10 per cent NH_4Cl the diammine may be formed as in equation (I), whereas for lower concentrations an oxychloride may be the principal reaction product:

$$4Zn + 8MnO_2 + 8H_2O + ZnCl_2 = 4Mn_2O_3 \cdot H_2O + ZnCl_2 \cdot 4Zn(OH)_2. \quad (II)$$

Obviously, the choice of reaction is dictated by such factors as diffusion effects, severity of service, degree of exhaustion of the cell system, and the like, and the transition from the first to the second can probably occur without inflection in operating voltage.

Final confirmation and extension of the early concepts is found in the important contribution by Copeland and Griffith (40) which established the formation of $ZnO \cdot Mn_2O_3$, the mineral occurring as hetaerolite, as a possible cathodic product. In this case, the over-all cell reaction may be written simply as

$$Zn + 2MnO_2 = ZnO \cdot Mn_2O_3 \quad (III)$$

in which no ammonium chloride is permanently removed from the cell system. Whereas the reaction as expressed by equation (I) requires two molecules of NH_4Cl per gram atom of zinc, the other two remove no sal ammoniac from the cell system; all of which emphasizes the difficulty of correlating cell composition with service capacity or of developing a single cell formulation that will give satisfactory service under all discharge conditions.

In view of the complex nature of the dry cell reaction it is not surprising that no entirely authoritative thermodynamic analysis has yet been presented. However, the work of Wadsley and Walkley (41) and the calculations of Kaneco (42), Thompson (43), and Drucker (44) as interpreted by Drotschmann (45) indicate voltages between 1.41 and 1.57 for the Leclanché system and represent at least an approach to the observed values.

Anode

Zinc, generally although not always amalgamated, is still almost exclusively used as anode metal in the dry cell. The anode reaction is relatively simple and uncomplicated. Even during continuous discharge, polarization or changes in concentration and *p*H of the anolyte have relatively slight effect on zinc potential (46), perhaps 0.2 volt at the current drain of flashlight service. It is the wasteful corrosion of zinc, rather than its anodic behavior in the operating cell, that has demanded the attention of the battery technologist, from the theoretical as well as the practical point of view.

In the early days of dry cell manufacture, minor constituents of zinc were considered in terms of the adaptability of the sheet metal to the manufacture of soldered cans; their effect on corrosion resistance seems long to have been a secondary consideration. Small quantities of lead and iron were, of course, always present, and cadmium was usually added to stiffen the sheet. The trend toward zinc of high purity, long advocated by Burgess (47) as a means of reducing wasteful corrosion, has been made possible by the introduction of drawn and extruded cans and the flat anodes now used in many cell constructions.

The intrinsic characteristics of the base metal with respect to corrosion are, of course, modified or obscured by the nature of the amalgamated zinc surface (48).

Mercury is generally introduced as $HgCl_2$ dissolved in the electrolyte, from which it is deposited on the zinc by replacement. The quantities of mercury that can be used effectively are very limited, particularly when the zinc is the cell container, seldom exceeding 0.25 per cent because of the embrittlement and loss of strength of the amalgamated metal. Even within the permissible range there is apt to be poor correlation between mercury concentration and resistance to corrosion (49), particularly at elevated temperatures (50). Obviously nature and uniformity of amalgamation are more important factors than slight variation in mercury concentration in building the surface of high hydrogen overvoltage requisite for resistance to corrosion.

In a properly constructed cell and in the absence of deleterious, e.g., heavy metal impurities, the corrosion of amalgamated zinc in standard NH_4Cl, $ZnCl_2$ electrolyte is slight

and, under normal storage conditions, dry batteries suffer relatively little loss in service capacity due to this factor. The situation is quite different for a cell in active use, where changes in anolyte *p*H and concentration, alteration of anode surface and actual loss of mercury from the latter during service, may introduce complicating factors. Even today, the wasteful corrosion of zinc in cells on long-time intermittent service may be as much as 50 per cent as great as the weight of metal utilized in generating current. This, in itself, is no small matter; it becomes even more serious if consideration is given to the fact that two moles of NH_4Cl are used up per gram atom of zinc

$$Zn + 2NH_4Cl = ZnCl_2 \cdot 2NH_3 + H_2, \qquad (IV)$$

involving a costly waste of active material and a direct loss of service capacity. In addition, the formation of the insoluble diammine causes a rise in internal resistance which further impairs the usefulness of the battery.

The problem of finding corrosion inhibitors, other than mercury, effective under the variable conditions of cell discharge and compatible with the standard dry battery ingredients, has not proved a simple task. The use of bichromates to form protective films on zinc has found successful commercial application (51). This expedient has undoubted beneficial effect on cells during storage, although its effectiveness under service conditions may be open to question. The liner itself, by its ability to maintain wet contact with zinc as well as by its composition, may have important influence on corrosion rate and some of the ingredients of cereal pastes themselves may be inhibitory in nature (52).

The better sealing of batteries, by exclusion of atmospheric oxygen, has markedly decreased zinc corrosion and, by preventing loss of moisture by evaporation, has made important contribution to service maintenance. Nevertheless, the rising cost of metal and other cell ingredients, and the demand for higher output levels and longer shelf life, the latter over an increasing temperature range, make further improvement imperative.

The search continues for anode materials other than zinc. Aluminum, with its high electrochemical equivalent (2.98 amp hr/g of metal as compared with 2.2 for magnesium and only 0.82 for zinc) would be an attractive substitute were it not for its high corrosion rate. It shows no voltage advantage over zinc in conventional electrolyte since in this medium it owes its stability, such as it is, to an oxide film and its true potential is not realized (53). Higher voltage can be obtained by amalgamation (54) or by the use of an electrolyte, either acid or alkaline, in which the oxide is soluble. In either case, the rate of corrosion of the base metal tends to become excessive.

The important progress which has been made in the utilization of magnesium anodes is discussed separately (56). This metal gives somewhat higher voltage than zinc [although not its true potential (57)], and its high rate of corrosion in electrolyte can be reduced by the use of inhibitors of the bichromate type and by substitution of bromides for chlorides (58). With the rapid strides in cell development made in recent years, the magnesium battery gives promise of achieving commercial significance in the not-too-distant future.

Electrolyte

Although the electrolyte of the original Leclanché cell was a saturated ammonium chloride solution [with an excess of solid salt in the battery jar (2)], the use of mixed sal ammoniac and zinc chloride electrolyte formed a part of very early dry battery technology (3). Unfortunately, the functioning of $ZnCl_2$ seems to have been understood only partially and the development of optimum electrolyte compositions proceeded largely on an empirical rather than on a scientific basis.

A definite forward step was marked by the work of Meerburg (59) in 1903, whose data on the solubility relationships of NH_4Cl and $ZnCl_2$, particularly when combined with conductivity (39) and specific gravity data, can be of great value in the compounding of mixes and pastes. These, however, are representative only of the fresh, unused cell, and throw little light on its service quality.

Once a cell is put into operation, the solution of zinc and lowering of *p*H at the anode, and the rise in *p*H at the cathode, complicate the solubility relationships. The change in anolyte is relatively simple, and the increase in zinc chloride concentration is within the scope of the Meerburg data. At the cathode, however, the electrolyte becomes a four-component system, in which NH_3 as well as $ZnCl_2$ and NH_4Cl (and H_2O) must be taken into account. This, further complicated by the shifting situs of reaction (60, 61), recuperation reactions, and the slow diffusion rates characteristic of the dry cell system has made study of electrolyte changes during discharge extremely difficult.

Definite progress toward the better understanding of the functioning of the electrolyte was made in the late 1920's, notably by Friess (62) who described the system $ZnCl_2$, NH_4Cl, NH_3, H_2O and correlated equilibrium data with *p*H measurements. His *p*H determinations were of necessity made with a hydrogen electrode and so could not be applied directly to the dry cell system. The introduction of the commercial glass electrode, and the development of rugged types, made possible measurements of electrolyte equilibria in isolated portions of mix and paste from actual cells under discharge conditions (39). On the basis of these studies, NH_4Cl is still to be considered the important electrolyte salt, whereas zinc chloride[6] serves primarily to reduce wasteful shelf corrosion and, by buffering the solution, to minimize *p*H changes.

The work on electrolyte equilibria has done much to give a significant explanation to variation in performance of the same cell under different discharge conditions. The problem of maintenance of *p*H within as narrow limits as possible, one of the criteria for optimum performance, may be of minor significance on light or intermittent drain, where ample time for diffusion and recuperation reactions is allowed; it becomes acute under conditions of heavy drain service. So it is that the bobbin of a "D" size cell on intermittent test (4-ohm LIF) becomes hard, due to formation of insoluble $ZnCl_2 \cdot 2NH_3$ and has no odor (mix *p*H perhaps 6–7). During continuous discharge, on the other hand, the mix may reach a *p*H of 9–10 and reek of ammonia, yet remain soft and friable because of the formation of the tetrammine, $ZnCl_2 \cdot 4NH_3$, relatively soluble in the alkaline electrolyte.

Despite a very considerable amount of work with other salts,[7] it seems significant that the combination of NH_4Cl and $ZnCl_2$ is still generally used in the dry cell built to meet conventional service demands. It is only for abnormal service conditions, and particularly where maximum capacity and

[6] $ZnCl_2$ does not, as frequently recorded in text books, significantly increase NH_4Cl solubility, nor does the hygroscopicity of the pure salt improve the moisture retention of the $NH_4Cl, ZnCl_2$ electrolyte composition used in the finished cell.

[7] Magnesium chloride (63) was used for many years in the German "Pertrix" battery. The Pörske patent (64) describing this development also mentions calcium chloride.

keeping quality are not absolutely essential, that the NH_4Cl, $ZnCl_2$ electrolyte has proved inadequate, and inferior to other compositions.

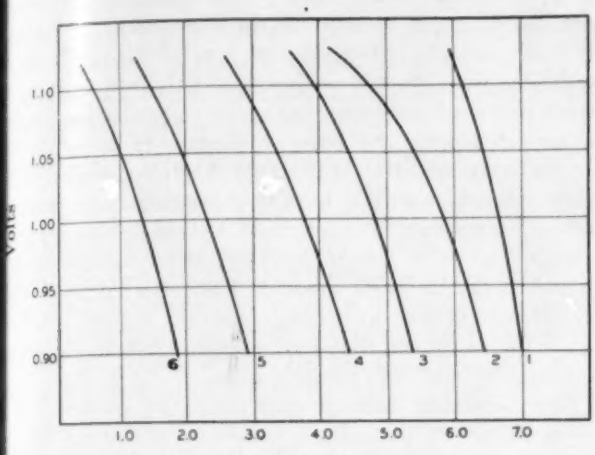

FIG. 1. Discharge characteristics of a "D" size flashlight cell:

Curve	Current drain in amp		
	*per cm² x 10^{-4}	per cell	per cm² anode area x 10^{-4}
1	5.5	0.03	7
2	11	0.06	14
3	16	0.09	21
4	22	0.12	28
5	36	0.20	47
6	55	0.30	71

* Calculation based on jacketed cell (volume 55.0 cc). For the unjacketed unit (volume 45.2 cc) values would be increased by 21.6 per cent.

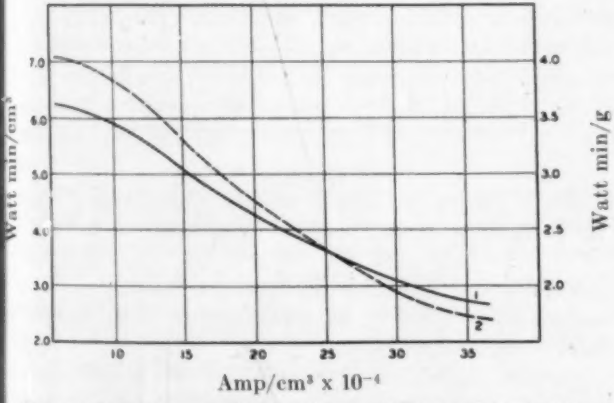

FIG. 2. Output per unit of volume (1) and weight (2) for a "D" size flashlight cell.

Low Temperature Electrolytes

The expanding usage of dry cells, particularly as reflected in military requirements, created a demand for batteries capable of operating at temperatures well below the freezing point (−6°F; −21°C) of the conventional NH_4Cl, $ZnCl_2$ electrolyte.

Vinal, whose recent text (65) contains a review of work on electrolytes for low temperature operation, points out that in general, the use of organic additions to depress the freezing point has not proved successful, primarily because of the low conductivities of the resulting solutions. The use of organic electrolytes such as monomethylamine hydrochloride (66), substitution of calcium chloride (67), wholly or in part, for zinc chloride, and the introduction of LiCl, $ZnCl_2$, NH_4Cl combinations (68) have given much better results. With these, cells can now be made which, although admittedly of lower service capacity than that obtained from conventional cells at room temperature, are still quite useful at temperatures of the order of −40°C.

Because of the importance of conductivity and diffusion in low temperature operation, the diaphragm or separator has also become an important factor, necessitating a re-examination of existing paste formulations. Locust bean gum, for example, is cited (69) as far superior to conventional starch: flour thickening agents in low temperature applications.

Depolarizer

The development of the dry cell and its rise to greater commercial importance than other primary battery systems have been due, in large measure, to an abundant supply of MnO_2 ores of depolarizer quality, high in oxygen content and sufficiently free from deleterious constituents to require little or no purifying treatment. In the early days of the dry cell, when availability and cost, rather than depolarizing effectiveness, usually dictated the choice of ores, the Russian Caucasus deposits furnished the bulk of the MnO_2 depolarizer for the commercial batteries of Europe and the U. S. The opening of mining operations at Philipsburg, Montana (70), produced a battery ore of superior quality and helped supply the industry during World War I when imports from Russia were cut off. Later the deposits on the Gold Coast district of West Africa (71) were developed and soon became the principal source of supply. Smaller amounts of battery grade ore have also been obtained from many other parts of the world, e.g., Cuba, Java, and Brazil.

A considerable amount of technical effort has gone into the development of forms of MnO_2 more active than the ores, either through the modification or beneficiation of ores by relatively simple treatment, or by the direct synthesis of MnO_2 by chemical or electrolytic precipitation methods. Leaching of ores with mineral acid (72), which decomposes carbonates and removes soluble constituents, produces a depolarizer of porous structure and increased available oxygen content. The so-called "activated ores" are obtained by more complex treatments such as the preparation of a lower oxide of manganese by roasting an MnO_2 ore to convert it to Mn_2O_3, followed by a leach with a mineral acid (73). The latter reaction may be represented as:

$$Mn_2O_3 + H_2SO_4 = MnO_2 + MnSO_4 + H_2O. \qquad (V)$$

Depolarizers of this type still find important uses in cell manufacture.

The use of synthetic depolarizer seems to have originated in Germany at a comparatively early date, presumably because of the availability of by-product MnO_2 as obtained, for example, in saccharin manufacture (74). Interest in the U. S. apparently developed somewhat later although, by 1910 or shortly thereafter, materials of local manufacture (75) as well as imported varieties were under active consideration. Substantially all known methods for the production of MnO_2 that seemed commercially practicable have been examined either here or abroad, these including the reduction of permanganate (76), the oxidation of manganous compounds by various reagents (19, 77), and even the thermal decomposition of salts like the nitrate (78). In the main, the gain in depolarizing activity and improvement in heavy-drain output of fresh cells with depolarizers so obtained was offset by nonuniform and generally unpredictable service

quality and by poor shelf characteristics. It was not until electrolytic MnO_2 (23) was produced in pure form on a commercial scale a little over ten years ago (24), that a really satisfactory synthetic depolarizer became available to the industry.

The cathodic reaction in the Leclanché dry cell, which contributes about one-half of the energy output of the system, continues to be an item of major technical interest. It consists, in its simplest terms, in the reduction of MnO_2, in which manganese is tetravalent, to an end product containing trivalent manganese. This means, of course, that only one-fourth of the oxygen content is utilized.

The actual reduction mechanism is neither simple nor, as yet, established with certainty. Two end products have definitely been established, one the mineral manganite ($Mn_2O_3 \cdot H_2O$), (79) the cathodic formation of which may proceed in accordance with the equation

$$2MnO_2 + 2NH_4^+ + 2e \rightarrow Mn_2O_3 \cdot H_2O + 2NH_3. \quad (VI)$$

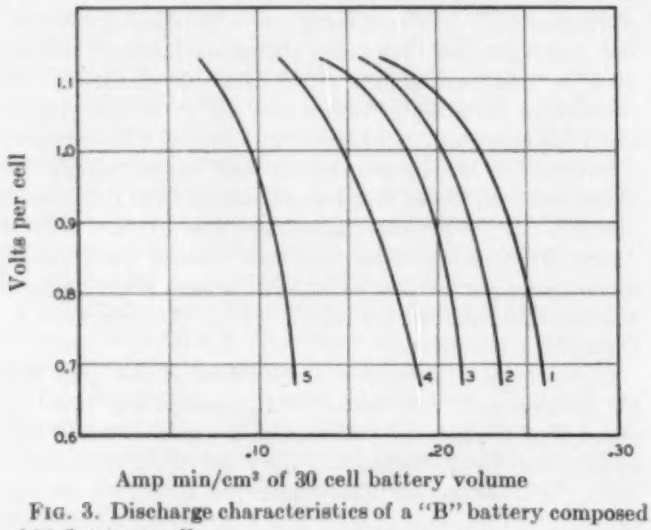

FIG. 3. Discharge characteristics of a "B" battery composed of 30 flat type cells:

Curve	Current drain in amp		
	per cm² x 10^{-6}	per battery	per cm² anode area x 10^{-6}
1	8.4	0.005	3.6
2	16.8	0.010	7.3
3	25.2	0.015	11
4	33.6	0.020	14
5	52.0	0.030	22

In the presence of zinc ion, a further reaction is possible (40, 80)

$$2MnO_2 + Zn^{++} + 2e \rightarrow ZnO \cdot Mn_2O_3 \quad (VII)$$

with the formation of the mineral hetaerolite. The latter is, of course, the more desirable reaction, removing no ammonium chloride from the system and entailing less rise in catholyte *p*H.

It is doubtful if any single problem in dry cell technology has claimed as much attention as the selection of manganese dioxide for depolarizer use. At first, so many factors militated against the realization of more than a small portion of the potential service capacity that the depolarizing effectiveness of the MnO_2 was not necessarily a dominating factor; as the battery was perfected and its field of usefulness expanded, the quality of the depolarizer became an increasingly important consideration. Chemical analysis, necessarily limited to determinations of available oxygen or of heavy metals and the like, although useful, gave little indication of the behavior of a depolarizer under battery conditions. Other methods included attempts to differentiate depolarizers on the basis of their catalytic effect on the rate of decomposition of hydrogen peroxide, the evolution of CO_2 from mixtures of MnO_2 and solutions containing oxalic and sulfuric acids (81) or oxygen equilibrium pressure changes as a sample was heated to convert it to Mn_2O_3 (82). Even magnetic susceptibility measurements (83) have been suggested as a means of differentiation but in most cases the impurities normally present, and other factors, have led to inconclusive results. Indeed, none of these methods has achieved more than limited success and, to this day, the only entirely definitive test is the costly and time-consuming evaluation of potential depolarizers in actual operating cells.

Electrochemical methods offer somewhat greater hope of success. The *pH*:potential relationship[8] of African ore, by way of example, in zinc and ammonium chloride solution may be represented by the equation

$$E = 1.070 - 0.0608\ pH$$

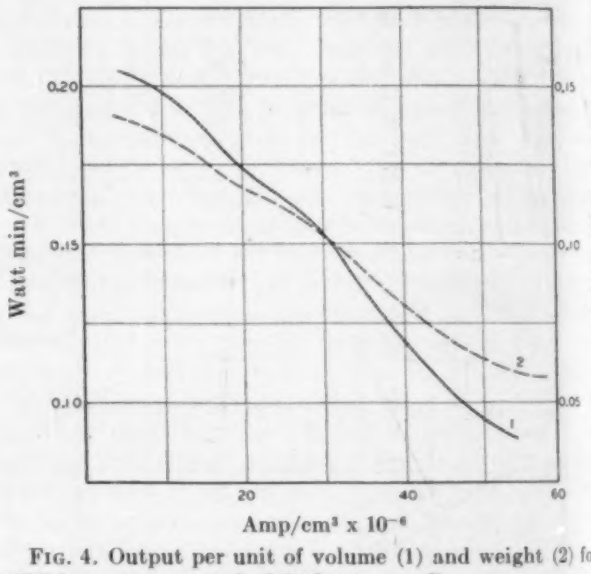

FIG. 4. Output per unit of volume (1) and weight (2) for a "B" battery composed of 30 flat type cells.

and deviations from this straight line function have been interpreted in terms of the suitability of MnO_2 samples for specific service applications.

A second method has been suggested (91) in which a direct measure of depolarizing capacity is obtained. In this, a sample of MnO_2 is reduced to a suitably chosen cut-off voltage in a stream of electrolyte which removes the cathodic by-products as they are formed. Although the efficacy of the MnO_2 so examined, in terms of the percentage of the available oxygen utilized in the electroreduction, is not an infallible

[8] Early measurements of MnO_2 potentials in various acid and alkaline solutions were reported by Tower (84) and by Thompson and Crocker (85). Daniels (86), working with MnO_2 electrodeposited on platinum wires, obtained a straight-line *p*H: potential curve approaching the theoretical slope. Thompson (87) obtained confirming results with both ores and artificial manganese samples. Parallel investigations by Holler and Ritchie (88) and by Martin and Helfrecht (89) failed to check these results, but it was later shown (90) that, with zinc chloride instead of HCl as acidifying medium, good correlation with theoretical slope (0.0598) could be obtained.

guide, it is generally indicative of service quality and makes possible the rejection of substandard materials.

The foregoing offers at least a clue to the cathodic reaction and the mechanism of the formation of $Mn_2O_3 \cdot H_2O$ (*vide supra*). Under test conditions Mn^{iv} is reduced to Mn^{ii}, the latter appearing in the cell effluent as $MnCl_2$. Mn^{ii}, in an operating dry cell, in turn might react chemically with the residual MnO_2 thus:

$$MnO_2 + MnCl_2 + ZnCl_2 \cdot 2NH_3 + 2H_2O \rightarrow Mn_2O_3 \cdot H_2O + ZnCl_2 + 2NH_4Cl. \quad \text{(VIII)}$$

Although this may satisfactorily explain the formation of manganite, now recognized as a cathodic byproduct, it gives no clue to the mechanism by which hetaerolite is produced.

X-ray diffraction methods, based on the earlier work of Dubois (92), Glemser (93), Drotschmann (94), and Schossberger (95) have already proved of value in the correlation of crystal structure of MnO_2 with its depolarizing effectiveness. Three allotropic forms of MnO_2, cryptomelane (α), pyrolusite (β), and ramsdellite (γ), (96) are now recognized. However, the problem has not been a simple one. With the possible exception of pyrolusite most of the available ores have been mixtures of poorly crystallized allotropes, hard to identify by physical appearance. Even when x-ray methods are used, the characteristic structure of the allotropes may be obscured or confused by variations in degree of crystallinity between samples of similar origin. McMurdie (97) applied electron microscope as well as x-ray techniques to differentiation of depolarizer samples and, with his adoption of the improved nomenclature of Fleischer and Richmond (96), did much to clarify a confused crystallographic situation. Delano (98) studied the effect of method of preparation on the crystal structure of the artificial product. According to this author many samples may be considered as imperfectly crystallized specimens since their x-ray patterns are intermediate between those of the pure allotropes. Cole, Wadsley, and Walkley (99) considered both synthetic and natural MnO_2 materials as possible mixtures of two or more allotropic forms and studied the crystal change from ramsdellite to pyrolusite resulting from thermal treatment[9] first described by Ramsdell (100).

As the result of this work, the current literature indicates ramsdellite to be the preferred MnO_2 modification for dry cell use. Our best ore (African) and our best synthetic oxide (electrolytic MnO_2) both show this crystal structure. The greater knowledge of manganese dioxide crystal types accumulated in this work promises to promote a wider application of x-ray diffraction methods both in the selection and in the most effective utilization of MnO_2 depolarizers.

No acceptable solid depolarizer for dry cells has yet been found that is competitive with MnO_2 on the basis of availability, cheapness, and activity. Graphitic oxide, which contains about 10 per cent available oxygen, has been proposed (102) but, so far as known, this depolarizer has not been used in commercial cells.

Air depolarization has perhaps come closest to providing a substitute for MnO_2. Both the French in World War I and the Germans, in turn, in World War II were faced with shortages of manganese and had to develop dry cells utilizing this expedient (103). As cathode material,[10] they used various forms of active carbon (107) with or without admixtures of conducting carbon or graphite, in pressed wet mix cakes sufficiently porous to permit air access. This is still current practice in Europe.

If provision is made for admission of air to a battery, desiccation and zinc corrosion are accelerated, and deterioration rate is sharply increased. This limits the usefulness of the cell. Though the air-depolarized dry cell has found a measure of commercial acceptance in Europe, the trend in the U. S. has been toward the alkaline system (108) rather than toward modifications of the Leclanché dry cell.

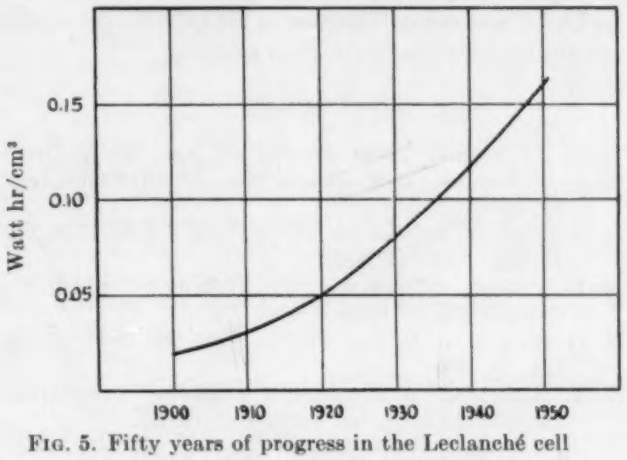

FIG. 5. Fifty years of progress in the Leclanché cell

* * *

As a review of the work of the last half-century on the dry cell, the present article is admittedly fragmentary[11] and inadequate. There are many omissions in material of both theoretical and technical interest that the reader, particularly the worker in the field, will notice, and coverage of excellent work done outside the U. S. is incomplete. The progressive rise in electrical output per unit of weight and volume; the variation of ampere and watt hour capacity with service conditions and its integration with current knowledge of cell reactions; the development and significance of present cell tests; these and a multitude of other items are deserving of detailed discussion rather than brief mention.

A separate chapter might be written on the once widely used reserve or "deferred action" batteries, inert and therefore not subject to normal deterioration during storage. In the more common forms of these, water, electrolyte (109) or zinc (110) was omitted or at least kept segregated (111) in the initial assembly, and activation was accomplished by adding the missing component. Nor would a dissertation be complete without a discussion, in the light of our present-day

[9] A differential thermal conductivity method (101) has been used (98) to explore further the crystal changes resulting from heating manganese dioxide. Though distinct differences between samples from different sources have been noted, no satisfactory correlation of these with depolarizer operation has yet been obtained.

[10] Even the ordinary manganese dioxide:carbon mix will operate as air depolarizing cathode. Leclanché (2) himself noted that his cell gave better performance when the electrode was only partially immersed in electrolyte, and Carhart (104) showed that as much as 50 per cent of the depolarization in the wet batteries might be due to air depolarization. Much of the early work on air depolarization was done with relatively inactive carbon containing small quantities of "accelerators," i.e., materials capable of electrochemical reduction, and subsequent regeneration by exposure to air (105). Since such additions were usually compounds of metals like nickel or copper which accelerate zinc corrosion, they have not proved adaptable to conventional cells of the Leclanché type, though still considered for use with alkaline electrolyte (106).

[11] A recent compilation, (113), lists over 3600 references to work done prior to 1948.

knowledge of the cell reactions, of the dry battery as a rechargeable unit (112).

The dry cell has come a long way during the life span of The Electrochemical Society. Due to the efforts of the industry to improve its product, electrical output per unit of volume has increased perhaps sevenfold within that period (see Fig. 5). The trend toward higher quality, well established by 1920, has become progressively more marked. The expanding field of usefulness for this small portable power unit and the current research interest in its potentialities suggest even greater advances in the years to come.

REFERENCES

1. F. B. Crocker, *Trans. Electrochem. Soc.*, **10**, 107 (1906).
2. G. Leclanché, *Les Mondes*, **16**, 532–5 (1868); *Compt. rend.*, **83**, 54–6 (1876).
3. C. Gassner, *German Pat.* 37,758, April 8, 1886; U. S. Pat. 373,064, Nov. 15, 1887.
4. D. Tomassi, "*Traité des Piles Électriques*," p. 267–271, Georges Carré, Paris (1889).
5. D. Misell, U. S. Pat. 603,112, April 26, 1898; 617,592, Jan. 10, 1899.
6. A. McQueen, "A Romance in Research," Instruments Publishing Co., p. 48, Pittsburgh (1951).
7. G. W. Heise, *Trans. Electrochem. Soc.*, **93**, 2–12 (1948).
8. M. Kemp, *New Edinburgh Phil. J.*, (1828) from P. Benjamin, "The Voltaic Cell," John Wiley & Sons, Inc., New York (1899).
9. S. R. Bottone, "Galvanic Batteries," p. 221 ff., Whittaker and Co., New York and London (1902).
10. W. L. F. Hellesen, U. S. Pat. 439,151, Oct. 28, 1890.
11. H. T. Johnson, U. S. Pat. 487,839, Dec. 13, 1892.
12. C. J. Coleman, U. S. Pat. 495,306, April 11, 1893.
13. G. W. Heise and E. A. Schumacher, U. S. Pat. 1,808,410, June 2, 1931; 1,890,178, Dec. 6, 1932.
14. W. B. Schulte, U. S. Pat. 1,370,054 and 1,370,055, March 1, 1921; G. W. Heise, U S. Pat. 1,788,870, Jan. 13, 1931.
15. A. W. Schorger, U. S. Pat. 1,316,597, Sept. 23, 1919, and 1,370,052, March 1, 1921; W. D. Staley, U. S. Pat. 1,760,090, May 27, 1930; G. W. Heise, U. S. Pat. 1,842,871, Jan. 26, 1932.
16. C. Hambuechen, U. S. Pat. 1,292,764, Jan. 28, 1919.
17. C. Hambuechen, *ibid.*; W. B. Schulte, U. S. Pat. 1,370,056, March 1, 1921.
18. N. C. Cahoon, U. S. Pat. 2,534,336, Dec. 19, 1950.
19. A. Heil, German Pat. 259,999 (1910); U. S. Pat. 1,053,390, 1,053,505, Feb. 18, 1913.
20. C. F. Burgess, U. S. Pat. 1,162,449, Nov. 30, 1915; 1,211,363, Jan. 2, 1917. (Cf. also McQueen (6), p. 182 ff.).
21. P. Burger, German Pat. 280,098 (1912); U. S. Pat. 1,123,843, Jan. 5, 1915.
22. W. R. Clymer, U. S. Pat. 1,480,533, Jan. 8, 1924; G. W. Heise, U. S. Pat. 1,553,530, Sept. 15, 1925.
23. G. W. Nichols, *Trans. Electrochem. Soc.*, **62**, 392 (1932); O. W. Storey, E. Steinhoff, and E. R. Hoff, *Trans. Electrochem. Soc.*, **86**, 337–45 (1944).
24. James A. Lee, *J.* (*and Trans.*) *Electrochem. Soc.*, **95**, 2*P*–13*P* (1949); also ref. (6) cf. Technical Appendix by O. W. Storey, p. 366.
25. A. Volta, *Phil. Trans. Roy. Soc.*, **90**, 403–31 (1800).
26. A. K. Huntley, *Trans. Electrochem. Soc.*, **68**, 219 (1935); C. J. Reed and M. T. Morrill, U. S. Pat. 690,772, Jan. 7, 1902.
27. H. F. French, *Proc. Inst. Radio Engrs.*, **29**, 299–303 (1941); U. S. Pat. 2,272,969, Feb. 10, 1942.
28. A. O. Franz, J. M. Martinez, and M. D. Koppelman, U. S. Pat. 2,416,576, Feb. 25, 1947.
29. O. K. Reinhardt, Canadian Pat. 341,637, May 15, 1934; R. R. Smith, U. S. Pat. 2,060,832, Nov. 17, 1936.
30. H. R. C. Anthony, U. S. Pat. 2,198,423, April 23, 1940.
31. R. F. Smith, U. S. Pat. 1,267,349, May 21, 1918; H. R. Palmer, U. S. Pat. 1,271,933, July 9, 1918; C. P. Deibel, U. S., Pat. 1,562,945, Nov. 24, 1925.
32. P. H. Adams, *Proc. Inst. Radio Engrs.*, (*Aust.*), **12**, 17 (1951).
33. *Trans. Electrochem. Soc.* (Discussion), **16**, 122 (1909); *ibid.*, **21**, 275 (1912).
34. American Standard Specification for Dry Cells and Batteries (Leclanché Type). *Circ. Nat. Bur. Standards C466*, Dec. 1, 1947.
35. S. R. Bottone, ref. (9), p. 51.
36. M. LeBlanc, "A Text-Book of Electrochemistry," The Macmillan Co., New York, p. 312 (1907).
37. A. W. Davidson, *J. Chem. Education*, **25**, 536 (1948); M. de K. Thompson and E. C. Crocker, *Trans. Electrochem. Soc.*, **27**, 155 (1915).
38. E. Divers, *Chem. News and J. Phys. Sci.*, **46**, 259–60 (1882).
39. N. C. Cahoon, *Trans. Electrochem. Soc.*, **92**, 159–72 (1947).
40. L. C. Copeland and F. S. Griffith, *Trans. Electrochem. Soc.*, **89**, 495–507 (1946).
41. A. D. Wadsley and A. Walkley, *Trans. Electrochem. Soc.*, **95**, 11–20 (1949).
42. S. D. Kaneco, *J. Soc. Chem. Ind. Japan*, **32**, 12 (1929); C. Drotschmann, ref. (45).
43. M. de Kay Thompson, *Trans. Electrochem. Soc.*, **68**, 167 (1935).
44. C. Drucker and R. Huettner, *Z. physik. Chem.*, **131**, 237 (1928); C. Drucker-A. Finkelstein, "Galvanische Elemente und Akkumulatoren," Akad. Verlagsges. m.b.H., Leipzig, p. 53 ff. (1934).
45. C. Drotschmann, "Moderne Primärbatterien," p. 11 ff. Nikolaus Branz, Berlin Schoenberg (1951).
46. N. C. Cahoon, ref. (39), p. 168.
47. Ref. (6), Technical Appendix by O. W. Storey, p. 364–5.
48. J. N. Friend, *Engineering*, **127**, 354–5 (1929) from C. A. **23**, 2372 (1929).
49. C. Drotschmann, *Helios*, No. 36 (1928) from ref. (45), p. 101.
50. G. W. Vinal, "Primary Batteries," p. 97, John Wiley & Sons, Inc., New York (1950).
51. R. C. Benner, U. S. Pat. 1,276,714, Aug. 27, 1918; O. E. Ruhoff, U. S. Pat. 1,331,877, Feb. 24, 1920; cf. ref. (6), Technical Appendix by O. W. Storey, p. 365 ff.
52. C. K. Morehouse, W. J. Hamer, and G. W. Vinal, *J. Research Nat. Bur. Standards*, **40**, 151 (1948).
53. J. V. Petrocelli, *J. Electrochem. Soc.*, **97**, 10 (1950).
54. A. J. Paine, *Electrician*, **72**, 258 (1913) from ref. (55).
55. W. R. Cooper, "Primary Batteries," p. 284, "The Electrician" Printing and Publishing Co., Ltd., London (1916).
56. C. K. Morehouse, *J. Electrochem. Soc.*, **99**, 187*C* (1952).
57. G. E. Coates, *J. Inst. Metals*, **71**, 457 (1945); B. Roath and W. Beck, *J. Electrochem. Soc.*, **98**, 277 (1951).
58. G. W. Heise, U. S. Pat. 1,899,615, Feb. 28, 1933; R. C. Kirk and A. B. Fry, *Trans. Electrochem. Soc.*, **91**, 277 (1948).
59. P. A. Meerburg, *Z. anorg. Chem.*, **37**, 203 (1903).
60. J. J. Coleman, *Trans. Electrochem. Soc.*, **90**, 545 (1946); *J. Electrochem. Soc.*, **98**, 26 (1951).
61. N. C. Cahoon and G. W. Heise, *J.* (*and Trans.*) *Electrochem. Soc.*, **94**, 214–219, 385–6 (1948); C. Drotschmann, *Chem. Ztg.*, **64**, 244–6 (1940).
62. R. Friess, *J. Am. Chem. Soc.*, **52**, 3085 (1930); F. Daniell, *Trans. Electrochem. Soc.*, **53**, 45–71 (1928).
63. C. Drotschmann, "Trockenbatterien," 3rd ed., p. 64 ff. Leipzig, (1945).
64. R. Pörske, U. S. Pat. 1,562,517, Nov. 24, 1925.
65. Ref. (50) p. 127 ff.
66. E. Otto, C. K. Morehouse, and G. W. Vinal, *Trans. Electrochem. Soc.*, **90**, 419, (1936).

67. N. Kameyama, and A. Naka, *J. Soc. Chem. Ind. Japan*, **39**, 432 (1936) from *C.A.* **31**, 4602 (1937).
68. M. E. Wilke, *Trans. Electrochem. Soc.*, **90**, 433 (1946).
69. Ref. (50) p. 146.
70. J. Pardee, *U.S. Geol. Surv. Bull. 725*, Washington, D. C., p. 146–147 (1922).
71. A. E. Kitson, *Am. Inst. Mining Met. Engrs.*, Tech. Paper 1622-C-1 (1927).
72. C. F. Burgess, U. S. Pat. 1,305,251, June 3, 1919.
73. C. F. Burgess, U. S. Pat. 1,305,250, June 3, 1919.
74. C. Drucker-A. Finkelstein, "Galvanische Elemente und Akkumulatoren," p. 72 ff., Akad. Verlagsges. m.b.H., Leipzig (1932).
75. Ref. (6) p. 179–183.
76. M. E. Holmes, U. S. Pat. 1,148,230, July 27, 1915.
77. M. L. Kaplan, U. S. Pat. 1,178,927, April 11, 1916.
78. M. L. Kaplan, U. S. Pat. 1,287,041, Dec. 10, 1918.
79. Ref. (39); also ref. (61); H. F. McMurdie, D. N. Craig, and G. W. Vinal, *Trans. Electrochem. Soc.*, **90**, 509–527 (1946).
80. Ref. (40); H. F. McMurdie, *Trans. Electrochem. Soc.*, **86**, 313–26 (1944).
81. O. D'Agostino, *Ricera sci.*, **9**, 195–206 (1938).
82. Z. Hermann and C. Slonim, *Monatsh.*, **70**, 84–103 (1937).
83. P. W. Selwood, R. P. Eischens, M. Ellis, and K. Wethington, *J. Am. Chem. Soc.*, **71**, 3039–3043 (1949).
84. O. F. Tower, *Z. physik. Chem.*, **18**, 17 (1895).
85. M. deKay Thompson and E. C. Crocker, *Trans. Electrochem. Soc.*, **27**, 155 (1915).
86. F. Daniels, *Trans. Electrochem. Soc.*, **53**, 45–71 (1928).
87. B. M. Thompson, *Ind. Eng. Chem.*, **20**, 1176–8 (1928).
88. H. D. Holler and L. M. Ritchie, *Trans. Electrochem. Soc.*, **37**, 607 (1920).
89. T. J. Martin and A. J. Helfrecht, *Trans. Electrochem. Soc.*, **53**, 83 (1928).
90. N. C. Cahoon, *Trans. Electrochem. Soc.*, **68**, 177 (1935).
91. N. C. Cahoon, *J. Electrochem. Soc.*, (in press).
92. P. Dubois, *Ann. chim.*, **5**, 411–482 (1936).
93. O. Glemser, *Ber.*, **72**, 1879 (1939).
94. C. Drotschmann, *Batterien*, **8**, 1082 (1940).
95. F. Schossberger, *Batterien*, **9**, 17–20, 33–35 (1940).
96. M. Fleischer and W. E. Richmond, *Econ. Geol.*, **38**, 269 (1943).
97. H. F. McMurdie, *Trans. Electrochem. Soc.*, **86**, 346 (1944).
98. P. H. Delano, *Ind. Eng. Chem.*, **42**, 523–7 (1950).
99. W. F. Cole, A. D. Wadsley, and A. Walkley, *Trans. Electrochem. Soc.*, **92**, 133–158 (1947).
100. L. S. Ramsdell, *Am. Min. J.*, **17**, 143 (1932).
101. L. H. Berkelhamer, *U. S. Bur. Mines, Tech. Pub. 664* (1945).
102. B. K. Brown, *Trans. Electrochem. Soc.*, **53**, 113–18 (1928).
103. C. Féry, *Electrician*, **80**, 320 (1917), from *C. A.* **12**, 565 (1918); *Compt. rend.*, **172**, 317–20 (1920).
104. F. Carhart, quoted by A. Nasarischwily, *Z. Elektrochem.*, **29**, 320 (1923).
105. L. Maiche, British Pat. 1,940, Oct. 24, 1882; Pollak and Wehr, French Pat. 170,411, July 31, 1885; A. von Welsbach, French Pat. 321,330, May 21, 1903; G. W. Heise (58); and many others.
106. K. Kordesch and A. Marko, *Oesterr. Chem. Ztg.*, **52**, 125–31 (1951).
107. Ref. (45), p. 158 ff.
108. E. A. Schumacher and G. W. Heise, *J. Electrochem. Soc.*, **99**, 191*C* (1952).
109. C. Drotschmann, Ref. (63), p. 360 ff.; R. C. Benner, U. S. Pat. 1,400,513, Dec. 20, 1921; R. C. Benner and H. F. French, U. S. Pat. 1,438,084, Dec. 5, 1922; G. W. Heise, U. S. Pat. 1,484,779–80, Feb. 26, 1924.
110. R. C. Benner, U. S. Pat. 1,438,085, Dec. 5, 1922.
111. H. F. French, U. S. Pat. 1,402,224, Jan. 3, 1922; 1,416,704, May 23, 1922.
112. K. A. Kobe and R. P. Graham, *Trans. Electrochem. Soc.*, **73**, 587–600 (1938); N. K. Chaney, *ibid.* (Discussion), p. 600 ff.
113. M. Bolen and B. H. Weil, "Literature Search on Dry Cell Technology," Georgia Institute of Technology, Atlanta, Ga. (1948).

Magnesium Primary Batteries

C. K. Morehouse[1]

During the last quarter of a century, production techniques have advanced until magnesium is now considered a common metal, competitive on the basis of cost and supply with such other metals as aluminum and zinc. Today it is extensively used in the structural fields, for cathodic protection, Grignard reactions, and metallurgical treatments. Another application which has been considered frequently during the last fifty years is its use as the soluble electrode or anode of primary batteries. The amount of magnesium now being used in primary batteries is small, but recent developments point to the possibility of magnesium finding extensive use in this field.

In Table I is given a comparison of some of the properties, together with a few theoretical calculations, of several of the more common metals which are now used as battery anodes or could conceivably be used. In making these calculations, it is assumed that the electrode efficiency is 100 per cent and that the electrode is not passivated during discharge, i.e., that it is able to operate at its reversible electrode potential. On the basis of watt-hour capacity per gram, sodium, aluminum, and magnesium are the most attractive. Sodium, however, is incompatible in aqueous solutions and aluminum has a definite disadvantage in that an oxide film is formed on the surface which passivates the electrode. If this oxide layer is removed, for example by amalgamation or by an alkaline treatment, the aluminum becomes very reactive and difficult to handle especially in the presence of aqueous solutions.

[1] Olin Industries, Inc., New Haven, Connecticut.

Historical

The theoretical advantages of magnesium as an anode for primary batteries were undoubtedly recognized even in the days of Volta. As early as 1887, Hein (1, 2) described a modified Bunsen cell which consisted of carbon and magnesium electrodes immersed in a nitric acid solution and magnesium sulfate. He also tried chromic acid as the magnesium electrolyte, but he reported unfavorable results. Hein makes reference to a modified Leclanché cell consisting of a magnesium anode, a manganese dioxide cathode, and an electrolyte of an aqueous solution of magnesium chloride or magnesium sulfate. However, little, if anything, of significance had been published on a magnesium Leclanché type cell up to the recent work of Kirk and Fry (3, 29).

From 1887 to about 1925 references to the use of mag-

nesium are infrequent and unimportant. Wood (4) in his 1928 patent describes a magnesium-manganese dioxide cell of either the wet or so called "dry" type, using an electrolyte comprising an aqueous solution of ammonium chloride, ammonium nitrate, and sodium dichromate. The inventor states that the dichromate and the nitrate provide a protective film on the surface of the magnesium which reduces the corrosion of the magnesium when the battery is not in use. Ferrabino (5, 6), an Italian, in his patents of 1930, describes magnesium cells with calcium sulfate and magnesium chloride electrolytes. In these patents reference is made to the use of such materials as calcium ferrocyanide as inhibitors to reduce the corrosion of magnesium. Manganese dioxide and lead dioxide coupled with magnesium were suggested as cathode material.

Gordon in his 1936 patent (7) describes a reserve-type multiple-cell magnesium battery comprising a loosely-fitted cellulose fibrous material as the separator, copper or silver as the positive electrode, magnesium as the negative electrode, and a solution of potassium iodide as an electrolyte. In his other 1936 patents (8, 10), he describes a magnesium air-cell type battery. This cell consisted of a carbon tube as the positive electrode and one or more magnesium pins, or rods of pure magnesium or of magnesium-aluminum-manganese alloys as the negative electrode. Aqueous solutions of calcium bromide or other halides were used as electrolytes. G. W. Heise (11) in his 1933 patent also describes a magnesium air-cell type battery.

Ruben (12) in his patent of 1933 describes a high-resistance magnesium potential cell containing an electrolyte composed of a glycol compound and a vanadium pentoxide cathode. In his patents (13, 14) issued in 1941 and 1942 in which a magnesium cell containing chromic acid electrolyte is described, Ruben points out that magnesium becomes passive in chromic acid, or alkali, or alkaline earth metal fluoride solutions. He found that, when one or more of these metal fluorides is added to the chromic acid, magnesium loses its passive character during current flow, but returns to it when not used if the proper fluoride is present in the correct proportion. He recommended an electrolyte of the following composition: 160 g chromic acid, 100 g water, 1 g magnesium fluoride.

Anderson (15), Forsythe (16), and Barbian and McNulty (17, 18) describe a primary cell with carbon and magnesium electrodes and a chromic acid electrolyte. Chromic acid solutions have some desirable features in that they dissolve the magnesium corrosion products formed during discharge and yet do not attack the magnesium itself. Barbian and McNulty found, however, that when chromic acid solutions were used alone as an electrolyte in the magnesium-carbon primary cell, the voltages were very low. By the addition of phosphoric acid and small concentrations of sulfate to the chromic acid electrolyte, the cell voltage and capacity were increased without excessively accelerating the open-circuit corrosion attack. The best electrolytes were: 40% chromic acid, 23% phosphoric acid, 37% water, and 40% chromic acid, 15% phosphoric acid, 0.01% sulfuric acid, 44.99% water. Cells of this type operated effectively at anode current densities of 3 amp/ft² (3 ma/cm²) and 1.0 to 1.5 v. This battery compares favorably with the Lalande type battery (zinc-copper oxide), but because of the larger quantity of electrolyte required per watt-hour, it does not compare so favorably with the air-depolarized battery.

Additional references to cells containing a magnesium anode and cathode of persulfate (19, 31) and magnesium (20) or calcium (21) permanganate are found in the literature. However, none of these electrochemical systems has been developed to date into a practical battery.

Practical Batteries

One of the first practical primary cells using magnesium as the negative electrode was the silver chloride-magnesium water-activated cell described in Harriss's patent (22) and by Mullen and Howard in their paper (23). A comparable battery, silver bromide-magnesium water-activated, is described in Lawson's patent (24, 25). This cell is the subject of a separate review paper by I. C. Blake. (See p. 000C.)

R. C. Kirk, A. B. Fry, and P. F. George of the Dow Chemical Company (3, 26–29) in their patents and papers described some of the efforts to develop a magnesium dry cell of the Leclanché type. This work, done under a Squier Laboratory Signal Corps contract, is the most significant development work which has been done leading toward a practical magnesium primary battery. They made a systematic and thorough study of alloy compositions, electrolyte compositions, and inhibitors. The alloy which gave the best results was AZ31A (3% aluminum, 1% zinc, 0.2% manganese, 0.15% calcium, and the remainder magnesium). Electrolytes consisting of aqueous solutions of alkali and alkaline earth bromides can be used, but magnesium bromide gave the best performance with respect to anode corrosion on shelf and cell capacity. Ammonium and lithium chromate inhibitors were also found to be effective in lessening the open circuit corrosion attack without affecting the discharge reaction.

The magnesium dry cells described by Kirk and Fry contained a cathode consisting of a mix of manganese dioxide-

TABLE I

Element	Electrode reaction	Reversible electrode potential	Density	Gram equiv weight	Metal req'd. per whr		Cost per lb†	Cost per kwhr*
					grams*	vol* (cc)		
Na	$Na^+ + e = Na$	−2.714	0.97	22.997	0.31	0.32	$0.17	$0.12
Mg	$Mg^{++} + 2e = Mg$	−2.34	1.74	12.16	0.19	0.11	0.25	0.10
Al	$Al^{+++} + 3e = Al$	−1.67	2.70	8.99	0.20	0.07	0.19	0.08
Zn (alkaline system)	$ZnO_2^= + 2H_2O + 2e = Zn + 4OH^-$	−1.316	7.14	32.69	1.0	0.14	0.18	0.40
Zn (acid system)	$Zn^{++} + 2e = Zn$	−0.761	7.14	32.69	1.6	0.22	0.18	0.63
Fe	$Fe^{++} + 2e = Fe$	−0.441	7.6	27.9	2.4	0.32	0.03	0.17
Cd	$Cd^{++} + 2e = Cd$	−0.402	8.65	56.2	5.2	0.60	2.55	29.2
Pb	$Pb^{++} + 2e = Pb$	−0.126	11.34	103.6	30.5	2.7	0.17	11.42

* Calculations based on hydrogen as other electrode.
† Cost is based on price of unfabricated metal.

acetylene black and electrolyte. The separator consisted either of starch-flour gel or of Kraft paper, the latter being preferred because of the increased capacity. This cell construction is in many ways identical with the present zinc Leclanché construction.

The current producing reactions of magnesium dry cells may be written as follows:

$$\text{Anode, } Mg \rightarrow Mg^{++} + 2e$$

$$\text{Cathode, } 2MnO_2 + H_2O + 2e \rightarrow Mn_2O_3 + 2OH^-$$

$$\text{Over-all, } Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2.$$

In their papers the authors presented results obtained on actual magnesium dry cells discharged on standard dry cell tests. They have shown that magnesium cells can be made to give double the capacity of comparable zinc batteries on such tests corresponding to flashlight, lantern, and radio applications.

There are, however, some problems which have to be solved before the magnesium dry cell as described supplants the zinc dry cell. A few of these are:

1. Magnesium cans cannot be drawn as easily as zinc cans and, although lighter in weight, are thicker than corresponding zinc cans. However, the results which Dow has obtained with impact extrusion of magnesium cans indicate that the manufacture of magnesium cans by the impact extrusion method is feasible. The difficulty is that most of the dry battery industry is equipped with zinc can-drawing equipment.

2. Another problem is the cleaning of the magnesium and the preparation of the surface. The following steps are necessary: (*a*) the lubricant used for coating the slug for impact extrusion has to be removed (using an alkaline solution); this is followed by (*b*) one or two pickling solutions which clean the surface and stabilize it. Presumably a chrome-type film forms over the metal which conditions it so that it is more resistant to corrosion.

3. A third problem which has been pointed out in the Kirk and Fry papers is that of delayed action. That is, when the circuit of the cell is closed, a few seconds are required for the magnesium cell to come up to operating voltage. This may present difficulties in certain applications.

4. Fourth, the high voltage of the magnesium cell may cause inconveniences. Most equipment is designed around the zinc Leclanché system and the introduction of a new cell which has a higher operating voltage will undoubtedly present a problem with respect to this equipment. It is conceivable that the solution may lie in lowering the cathode voltage of the cell or increasing the internal resistance of the battery.

5. Finally, magnesium cans cannot be satisfactorily soldered to give good intercell connections. However, stranded wire has been spot-welded successfully to the magnesium cans.

The problems as listed above are not believed unsolvable and, in fact, the development of a magnesium dry cell has progressed to the stage that extensive field tests are being conducted by the military (30).

REFERENCES

1. G. Hein, *Elektrochem. Z.*, **8**, 472, 517 (1887).
2. R. Fichter, *Chimia*, **1**, 141 (1947).
3. R. C. Kirk and A. B. Fry, *J.* (*and Trans.*) *Electrochem. Soc.*, **94**, 277 (1948).
4. R. T. Wood (to American Magnesium Corp.), U. S. Pat. 1,696,873, Dec. 25, 1928.
5. G. Ferrabino, Swiss Pat. 137,015, March 1, 1930.
6. G. Ferrabino, Swiss Pat. 137,016, March 1, 1930.
7. C. J. Gordon, U. S. Pat. 2,040,255, May 12, 1936.
8. C. J. Gordon, U. S. Pat. 2,050,172, Aug. 4, 1936.
9. J. W. Smith, *Light Metals*, **1**, 172 (1938); **9**, 354 (1946).
10. C. J. Gordon, British Pat. 526,601, Dec. 12, 1940.
11. G. W. Heise (to National Carbon Co.), U. S. Pat. 1,899,615, Feb. 28, 1933.
12. S. Ruben, U. S. Pat. 1,920,151, July 25, 1933.
13. S. Ruben, U. S. Pat. 2,257,129, Sept. 30, 1941.
14. S. Ruben, U. S. Pat. Re. 22,053, March 24, 1942.
15. E. L. and L. B. Anderson, U. S. Pat. 2,530,751, Nov. 21, 1950.
16. W. R. Forsythe (to Dow Chemical Co.), U. S. Pat. 2,301,390, Nov. 10, 1942.
17. H. A. Barbian and R. E. McNulty, *Trans. Electrochem. Soc.*, **91**, 387 (1947).
18. H. K. DeLong and H. A. Barbian (to Dow Chemical Co.), U. S. Pat. 2,481,204, Sept. 6, 1949.
19. G. Polcich, U. S. Pat. 1,771,190, July 22, 1930.
20. D. V. Louzos (to Burgess Battery Co.), U. S. Pat. 2,535,742, Dec. 26, 1950.
21. P. Matarazzo, Italian Pat. 190,791, Sept. 13, 1907.
22. L. H. Harriss (to Burgess Battery Co.), U. S. Pat. 2,543,106, Feb. 27, 1951.
23. J. B. Mullen and P. L. Howard, *Trans. Electrochem Soc.*, **90**, 529 (1946).
24. H. E. Lawson (to Burgess Battery Co.), U. S. Pat. 2,428,850, Oct. 14, 1947.
25. H. E. Lawson, U. S. Pat. 2,445,306, July 13, 1948.
26. A. B. Fry, R. C. Kirk, and P. F. George (to Dow Chemical Co.), U. S. Pat. 2,547,907, April 3, 1951.
27. A. B. Fry, R. C. Kirk, and P. F. George (to Dow Chemical Co.), U. S. Pat. 2,547,908, April 3, 1951.
28. P. F. George, A. B. Fry, and R. C. Kirk (to Dow Chemical Co.), U. S. Pat. 2,547,909, April 3, 1951.
29. R. C. Kirk, P. F. George, and A. B. Fry, *J. Electrochem. Soc.*, **99**, 323 (1952).
30. *Business Week*, p. 67, April 26, 1952.
31. I. C. Blake and J. B. Mullen (to Burgess Battery Co.), U. S. Pat. 2,534,403, Dec. 19, 1950.

The Alkaline Manganese Dioxide Dry Cell

W. S. Herbert[1]

Alkaline wet cells employing manganese dioxide as depolarizer were proposed as early as 1882 (1) and again in 1903 (2). Dry cells of this type were first described in 1912 (3) and were studied sporadically up to 1936 (4–8). As far as can be learned none of these early cells attained any form of commercial success. Renewed interest in all kinds of alkaline dry cells has been stimulated in recent years by the outstanding development of mercuric oxide dry cells by Ruben (9, 10) and their ensuing successful manufacture on a large commercial scale. In 1949, batteries containing new type cells using the alkaline-manganese dioxide system were first produced on a commercial basis.

The alkaline-manganese dioxide cells[2] now on the market are called "crown" cells because of the use of crown-type caps. The construction is shown in cross-sectional view in Fig. 1.

The manganese dioxide-graphite depolarizer mix (usually about 10:1 ratio) is pressed into a steel can which is spot-welded to the steel positive cap. A porous felt-type cellulosic separator holds the electrolyte in immobilized form and serves as a spacer between the anode and cathode. Amalgamated powdered zinc is pressed into the plastic ring and in contact with the tinplate negative cap to form a porous anode. The aqueous electrolyte is about 30 per cent sodium

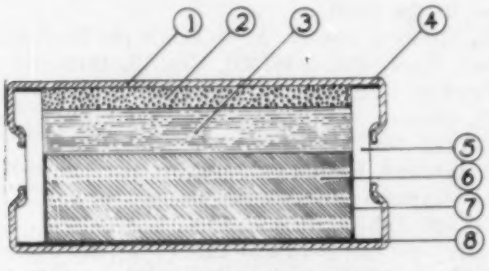

FIG. 1. Cross-sectional view of an alkaline crown cell. 1—tinplate negative cap, 2—zinc powder anode, 3—absorbent separator, 4—sealing material, 5—plastic ring, 6—depolarizing mix, 7—steel mix can, 8—steel positive cap.

hydroxide containing sufficient dissolved zinc to suppress the chemical solution of the zinc. Because the depolarizer is insoluble in the electrolyte a diaphragm or barrier layer is not required. The cell is sealed tightly by crimping the end caps over the shoulders of the plastic ring, thereby compressing the resilient sealing material.

Upon discharge of the cell, the following reactions occur:

at the anode,

$$Zn \rightarrow Zn^{++} + 2e$$

$$Zn^{++} + 2OH^- \rightarrow ZnO + H_2O$$

at the cathode,

$$2MnO_2 + H_2O + 2e \rightarrow Mn_2O_3 + 2OH^-.$$

The cell has a potential of about 1.52 volts. The zinc anode is converted to a paste type of zinc oxide which varies from white to blue with increasing current density. During use, the depolarizer increases in volume and changes from black to brown, becoming a reddish-orange when the conversion to Mn_2O_3 is complete. Although the electrolyte is not changed during discharge, both the depolarizer and zinc oxide absorb electrolyte during use so the cell has the desirable feature of becoming virtually dry and nonleaking after use. Because the reactions occur with almost 100 per cent efficiency at moderate and low drains the cell has a high capacity per unit volume.

The alkaline crown-type cells are now being made in two sizes which are used in several battery designs. The cells are

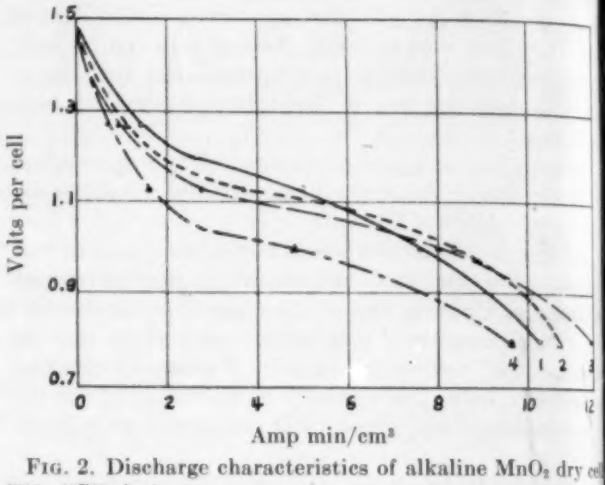

FIG. 2. Discharge characteristics of alkaline MnO_2 dry cell (500- "C" size):

Curve no.	Constant current drain	Current density		ma/cm² electrodes
		Amp/cm³	Amp/in.³	
1	0.25ma	.00037	.0061	0.32
2	0.50ma	.00075	.012	0.63
3	0.75ma	.0011	.018	0.95
4	1.50ma	.0022	.037	1.90

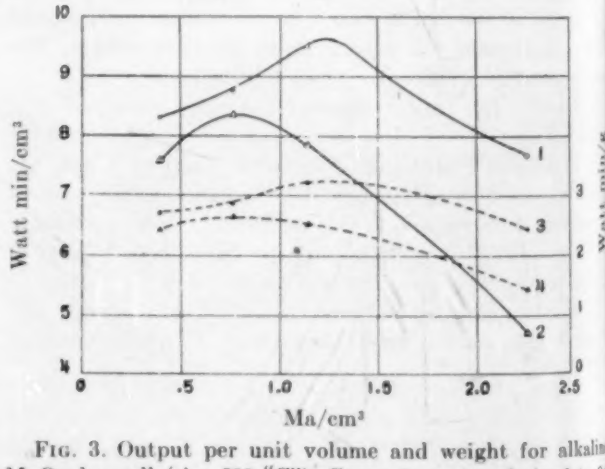

FIG. 3. Output per unit volume and weight for alkaline MnO_2 dry cell (size 500 "C"). Curve 1—watt min/cm³ to 0.8 v/cell; curve 2—watt min/cm³ to 1.0 v/cell; curve 3—watt min/g to 0.8 v/cell; curve 4—watt min/g to 1.0 v/cell.

assembled in series for batteries by simple stacking and enclosure in a suitable plastic or insulated metal shell. The 500-"C" size of 0.67 cm³ (0.041 in.³) is used mostly for miniature hearing-aid "B" batteries for applications involving drains up to about 2 ma. The smaller 600-"D" size of 0.55 cm³ (0.034 in.³) is used in subminiature hearing-aid "B" batteries for drains up to about 1 ma. A larger size

[1] Ray-O-Vac Company, Madison, Wisconsin.

[2] Matter subject of patent applications.

e 900-"C", of 2.23 cm³ (.136 in.³) is being made for portable dio and large size hearing-aid "B" batteries for drains up about 15 ma.

Typical performance curves for the 500-"C" size are given Fig. 2 and 3.

The alkaline-manganese dioxide cells being produced were signed for low-drain applications such as those given bove. However, it is possible to vary the constituents for pecial applications so that much heavier drains can be andled. Because of the effective seal, the shelf life of these ells is good and there is little or no loss of capacity on elayed tests.

REFERENCES

1. Leuchs, German Pat. 24,552 (1882).
2. S. Yai, U. S. Pat. 746,227 (1903).
3. E. Achenbach, German Pat. 265,590 (1912).
4. E. Achenbach, German Pat. 279,911 (1913).
5. A. Heil (to C. Hubert & S. Stern), U. S. Pat. 1,195,677 (1916).
6. F. Böcker and A. Eichoff, German Pat. 343,336 (1918).
7. N. Malichatka, German Pat. 456,423 (1926).
8. Piles Wonder, French Pat. 793,617 (1936).
9. S. Ruben, *Trans. Electrochem. Soc.*, **92**, 183 (1947).
10. M. Friedman and C. E. McCauley, *Trans. Electrochem. Soc.*, **92**, 195 (1947).

The Alkaline Cell with Copper Oxide or Air Depolarization (1902-1952)

***Erwin A. Schumacher*[1] *and George W. Heise*[1]**

The use of solid depolarizers in galvanic cells was first disclosed in 1843 by de la Rive (1), but it was not until 1881 that de Lalande and Chaperon (2) devised the first practical battery employing copper oxide in aqueous caustic alkali electrolyte in combination with a zinc anode. The Cupron cell (3) in Germany, and the Neotherm unit (4) in England were followed in due course by the Edison (5), Waterbury (6), and Columbia modifications (7) in the United States. Though long-sought (8), the substitution of an air-depolarized cathode for the copper oxide, whereby operating voltage was approximately doubled, was not successfully accomplished (9) until some forty years after the introduction of the Lalande element.

The alkaline elements have become the most important of present-day primary wet cells. Their greatest usefulness is found in applications in which large capacity, ability to deliver moderately large currents at constant voltage, and long life are the dominant service requirements. They are well suited, therefore, for mine, highway, railway, and marine signalling installations, for telephone and telegraph circuits, for radio "A" and various other uses where they may be employed either as the direct source of electrical energy, or as stand-by to furnish current in the event of power-line failure. More than 1.5 million Lalande cells are produced annually in the U. S. alone, ranging in capacity from about 75 to 1000 amp-hr and with current output as high as 15 to 20 amp for the largest units. A 500 amp-hr size capable of 2 to 3 amp discharge rate is most common. Fewer air-depolarized cells are made at the present time but, with the advantage of substantially higher voltage and lower critical material requirement, their commercial importance is rapidly increasing.

Copper Oxide Cells

The anode reactions taking place during discharge of the copper oxide-alkali-zinc cell are relatively simple. Zinc in 5*N* to 6*N* caustic soda electrolyte[2] is oxidized anodically with formation of zincate ions (10) in accordance with reactions of the general type

$$Zn \rightarrow Zn^{++} + 2e \qquad (I)$$

$$Zn^{++} + 3OH^- \rightarrow HZnO_2^{-*} + H_2O. \qquad (II)$$

Except at very high current densities, the zinc electrode behaves very nearly reversibly (3). In a 5 to 6*N* solution, free from dissolved zinc, it has a potential of −1.32v referred to the standard hydrogen electrode (11).

Upon saturation of the electrolyte with zinc, crystals of octahedral zinc hydroxide (VI) form on the electrodes and container walls, usually in adherent, impervious layers, to terminate cell operation. Under special conditions of discharge, amorphous deposits of zinc oxide may be formed, and long, needle-like crystals of sodium zincate may be observed in cells at low temperature.

A commercial 500 amp-hr battery requires about 4.4 liters (equivalent to nearly 9 ml/amp-hr) of 5 to 6*N* caustic soda electrolyte. This concentration represents the range of maximum conductivity and minimum freezing point,[3] and is therefore preferred over more concentrated solutions (6), even though the latter can dissolve more zinc (12) at room temperature and give correspondingly higher capacity.

The electrochemical reduction of the copper oxide cathode is generally thought of as taking place in two steps, (13)

$$2CuO + 2e \rightarrow Cu_2O \qquad (III)$$

$$Cu_2O + 2e \rightarrow 2Cu. \qquad (IV)$$

However, cupric oxide can react chemically with metallic copper to form an intermediate oxide

$$CuO + Cu \rightarrow Cu_2O \qquad (V)$$

and, after the initial stages of discharge, equation (IV) may be assumed to be the principal cathode process. The over-all cell reaction can be written as

$$3Zn + 3CuO + 2NaOH \rightarrow Na_2Zn_2O_3 + 3Cu + Zn(OH)_2. \qquad (VI)$$

The potential of the copper oxide electrode referred to the standard hydrogen electrode is −0.26 (14); therefore with a zinc potential of −1.32 the corresponding cell value for the

[1] National Carbon Research Laboratories, Cleveland, Ohio.

[2] An important advantage of sodium hydroxide over caustic potash is its substantially lower cost.

[3] A 6.0*N* solution of sodium hydroxide has a specific conductance of 0.33 ohm⁻¹/cm at 18°C, and a freezing point of −28°C.

* Hantzsch (10) assigns the formula $NaHZnO_2$ to the zinc complex; the latter may also be written $Na_2Zn_2O_3$ ($2NaHZnO_2 = Na_2Zn_2O_3 + H_2O$).

copper oxide-alkali-zinc system initially is 1.06 v. Voltages up to 1.24 have been reported (6) but since these are not reproducible and disappear rapidly in the first stages of discharge, it has been assumed that they are due to oxygen sorbed on the copper oxide or initially dissolved in the electrolyte.

Under normal discharge conditions,[4] the operating voltage varies between 0.5 and 0.7 v. Performance characteristics for a conventional 500-amp-hr cell are shown graphically in Fig. 1 and 2. Potential drops with temperature, and below 0°F (−18°C), a cell becomes inoperative at all but the

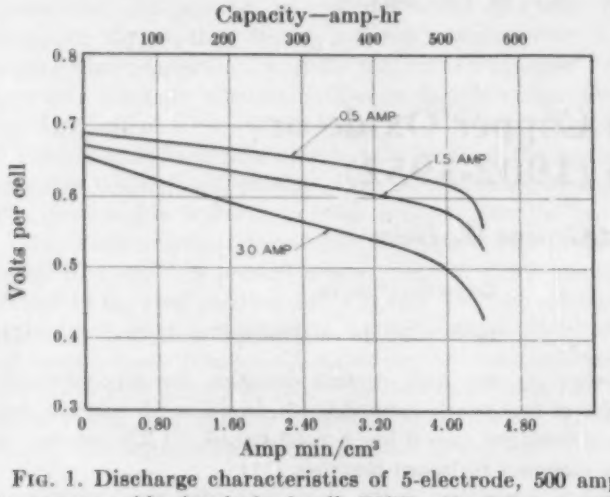

FIG. 1. Discharge characteristics of 5-electrode, 500 amp-hr, copper oxide depolarized cell (70°F). (At 1.5 amp, the electrode current density is approximately 3.1 amp/ft² or 0.33 amp/dm².)

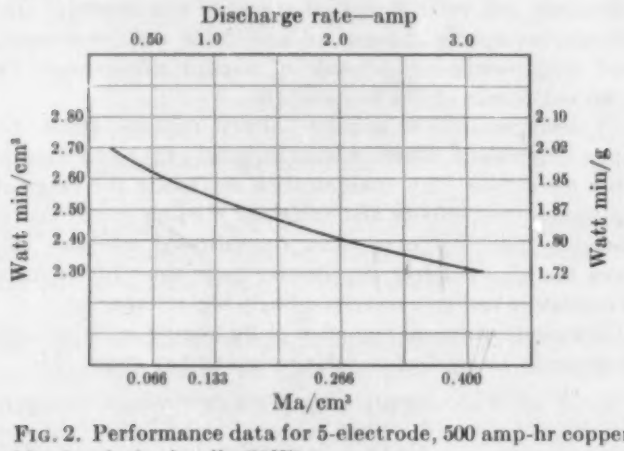

FIG. 2. Performance data for 5-electrode, 500 amp-hr copper oxide depolarized cell (70°F).

lowest current densities. For railway signalling applications, the minimum safe operating temperature is set at about 25°F (−4°C), protection against lower temperature being provided by housing the cells in underground wells.

Several forms of the Lalande cell are in current use. The zinc and agglomerated copper oxide electrodes are usually flat and rectangular (Fig. 3), less frequently annular (6) in shape. Mechanical support and electrical connection to the external positive terminal are obtained by mounting the oxide plates in steel frames, the latter giving support also to the insulating members from which the zinc anodes are suspended. Because exhausted electrolyte is heavy and accumulates at the bottom of the container, it is customary to place the electrode assembly as high in the battery jar as is practicable (6). Cell capacity is determined primarily by the solubility of zinc in the electrolyte and therefore by the volume of the latter.

The number of electrodes per cell varies according to service drain requirements. Usually three (two zinc anodes, one copper oxide cathode) or five (three anodes, two cathodes) are sufficient, but up to thirteen may be employed in heavy-duty cells. In commercial practice, the anode-cathode assemblies are shipped as units, the caustic soda being packed in separate, water-tight containers. Electrolyte preparation and final cell assembly are carried out in the field. For reasons of economy, the weights of anode and depolarizer material are regulated to give an ampere-hour output only slightly in excess of the battery rating and considerable care is exercised to maintain the active ingredients in balanced relationship.

FIG. 3. Five-electrode assembly for 500 amp-hr copper oxide railway signal cell.

The use of granular copper oxide is still practiced. In some early cells (17), the depolarizer was placed loosely on a metal plate at the bottom of the cell container. In a current modification, the oxide is packed into a perforated, paper-lined (18) rectangular steel basket with a central metal vane connecting the oxide to the positive terminal. The oxide may be treated with a small amount of sulfur (19) which raises the operating voltage of the cell by about 0.10 to 0.15 v. This higher voltage provides a factor of safety in the operation of track circuits, when ballast resistance is lowered by moisture.

As in the earliest forms of the Lalande unit (20), the copper oxide plates of present-day cells may be formed by agglomerating the powdered oxide with a suitable binder, e.g., caustic soda or a silicate. A mixture of cupric sulfate, caustic soda, and copper oxide (21) is said to produce a particularly strong agglomerate. Whichever binder is used, the mixtures are compressed and subsequently baked at high temperature, e.g., 1200°–1750°F, to complete the bonding action. Because of the relatively poor electrical conductivity of the finished electrodes—only partially corrected by the steel suspension frames—it is common practice to heat the

[4] In view of the range of sizes of commercial cells, and the complexity of service requirements, detailed discussion of discharge characteristics is considered beyond the scope of the present paper. Test specifications for railway type cells have been prepared by the Association of American Railroads (15); typical discharge curves are given by M. L. Martus (6), and G. W. Vinal (16).

plates in a reducing atmosphere (22) to produce a superficial, conducting layer of metallic copper. Alternatively, zinc or aluminum may be sprayed or painted on the oxide surface to effect reduction when the electrodes are immersed in electrolyte. Such coatings are said to be insufficiently adherent or stable to be completely reliable (6) and it has been proposed instead to connect the negative and positive electrodes with a piece of zinc wire which, on contact with electrolyte, causes a short circuit of limited duration to give the desired reduction.

Depending on the configuration of the positive electrode, the anodes are cast either as plates or cylinders. Zinc of the highest possible purity (6) is used. For maximum stability in the electrolyte, mercury is added to the extent of 0.5–2.5 per cent of the anode weight, either by incorporation during the zinc melting operation or by surface amalgamation. Zinc corrosion is almost theoretical during discharge. However, due to the solubility of the copper oxide in the caustic electrolyte, copper may be deposited on the anode by displacement during periods of idleness, and considerable wasteful corrosion may result.

For commercial cells, particularly those used by the railroads, a visual indication of approaching cell exhaustion is desirable to enable the maintainer to anticipate replacement. For this purpose "drop-out" panels of predetermined thickness are located either at the bottom edge (23) or in the body of the zinc plate (11), or the entire surface of the anode may be designed to develop characteristic patterns at stipulated service stages (16). Indicator panels of different thicknesses (23) may be used to mark the approach to the delivery of rated capacity.

The granular caustic soda ordinarily used in the Lalande cell is preferably of a high order of purity (6) and the electrolyte prepared from it generally is made with water of potable quality. Because the preparation of solutions with powdered alkali may be accompanied by dusting, it is customary to furnish the material in the form of flakes or small cubes. Dusting may be avoided, even with powdered soda, by mixing oil with the alkali before it is packaged for shipment. Solution of the caustic releases the oil which rises to form a seal over the solution surface. Such oil seals protect the solution against adsorption of carbon dioxide and evaporation of water.

Oil is more commonly supplied in separate glass containers. It should be of medium viscosity, free from saponifiable material and with a surface tension such that creepage of electrolyte and formation of carbonate crystals (15) on the top of the cell are prevented. Attempts also have been made to put the oil into electrolyte soluble capsules, shipped in the caustic soda container (24). In cells employing granular copper oxide, the oil has been incorporated in the depolarizer mass (25), floating to the top when the assembly is immersed in the freshly prepared, hot electrolyte.

Air-Depolarized Cells

Replacement of the copper oxide electrode of the Lalande cell[5] with a cathode capable of utilizing atmospheric oxygen results in a cell (open-circuit voltage, 1.45–1.50 v) of twice the operating voltage of the Lalande unit and frees it from many of the limitations of a solid chemical depolarizer. It is not surprising, therefore, that efforts to develop commercial air-depolarized batteries should have been made at an early date. Perhaps the most ambitious of these was the Walker-Wilkins cell (27) patented in 1894 (28) in which zinc and the bulk of the electrolyte were placed in a porous pot surrounded by granular carbon. The carbon, kept moist by caustic soda solution trickling through the porous container, served as cathode. The difficulty of maintaining a system of this type in good operating condition and, no doubt, the low depolarizing activity of the carbon led to the early withdrawal of this cell from the market.

In other attempts as well, lack of suitable carbon continued to be a major obstacle to success. In much of the earlier work (29) and, for that matter, even in rather recent developments (30), "accelerators," e.g., metal oxides capable of electrochemical reduction and subsequent chemical regeneration by oxygen, have been employed in small amounts to enhance depolarizing activity or to permit the use of relatively inert carbon or graphite.[6] With the development of active carbons, these "catalyzed" carbons have assumed a role of minor importance.

The electrochemical behavior of the cathode carbons currently employed is determined by their structure and the amounts and nature of their carbon:oxygen surface complexes (32). Peroxidic or peracidic linkages are indicated, their form depending on the thermal treatment of the carbon (33). Exposed to air, the active carbons acquire various amounts of both physically and chemically-sorbed oxygen and, in contact with aqueous electrolyte, they develop reproducible potentials. Because of their marked oxidizing properties (34), they have been applied not only to electrochemical depolarization, but also to "catalytic" chemical oxidations with air or oxygen (35).

It seems definitely to have been established (36) that the cathode reaction in alkaline electrolyte is based on the reversible equilibrium with peroxyl ion:

$$O_2 + H_2O + 2e \rightleftharpoons OH^- + HO_2^- \qquad \text{(VII)}$$

and that the final product is peroxide

$$OH^- + HO_2^- + 2Na^+ \rightarrow Na_2O_2 + H_2O. \qquad \text{(VIII)}$$

Equation (VIII) demands twice as much oxygen per faraday as is normally observed in an operating battery. This apparent anomaly finds ready explanation in the instability of peroxide in the presence of active carbon, and it is only at low temperatures and high current densities that oxygen consumption approaches the theoretical value[7] (37). Weiss and Jaffe have shown (36) that peroxide in caustic alkali electrolyte does not act as primary depolarizer, any beneficial effects associated with its presence resulting from liberation of oxygen at the carbon:electrolyte interface.[8]

The cathodes now in general use are made of amorphous carbon (40) in agglomerated rather than in granular or in powdered form (41). The finished electrode should be per-

[5] In the form of the Wedekind element (26), a Lalande cell was so designed that the copper oxide cathode of an exhausted cell could be removed and regenerated by heating in air. This might perhaps also be considered a form of air depolarization although of course neither continuous, nor effective at the voltage of the oxygen electrode.

[6] The proposal has also been made (31) to combine the functions of both copper oxide and carbon black in a single electrode, the former designed to act as depolarizer when the black becomes overloaded.

[7] The over-all cell reaction may therefore be expressed in form similar to that used for the Lalande cell (VI):

$$3\,Zn + \tfrac{3}{2}\,O_2 + 2NaOH \rightarrow Na_2Zn_2O_3 + Zn(OH)_2 \qquad \text{(IX)}$$

[8] Various tests have been proposed (38) for the evaluation of battery carbon, among them the correlation of rate of hydrogen peroxide decomposition with depolarizing quality (39). Such factors as fineness and presence of impurities themselves catalytically active throw doubt on the results of such measurements.

meable to air[9] but substantially impervious to electrolyte. A mild waterproofing treatment, e.g., impregnation with wax, grease, rubber (42), or other water-repellent substances in volatile solvents, should reduce the penetration of caustic alkali electrolyte to a few millimeters per year (43).

Since the volume of oxygen required in air depolarization is fairly large (approximately 4 cc of oxygen or 20 cc of air per minute for one-ampere drain), air access must be facilitated, either by making the surface exposed to air as large as possible, or by reducing the distance from breathing surface to the electrochemically active cathode:electrolyte interface.

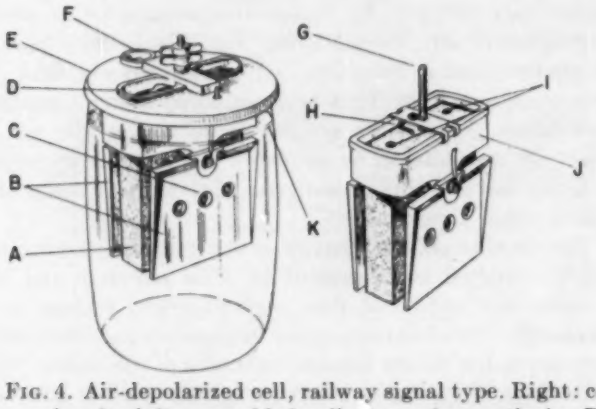

FIG. 4. Air-depolarized cell, railway signal type. Right: cell renewal unit; left: assembled cell. A—carbon cathode; B—zinc anodes; C—exhaustion indicator panels; D—breather opening; E—porcelain cover; F—filler opening for oil; G—movable suspension bolt; H—flexible cable cathode connection; I—carbon ventilating openings; J—plastic collar; K—oil layer.

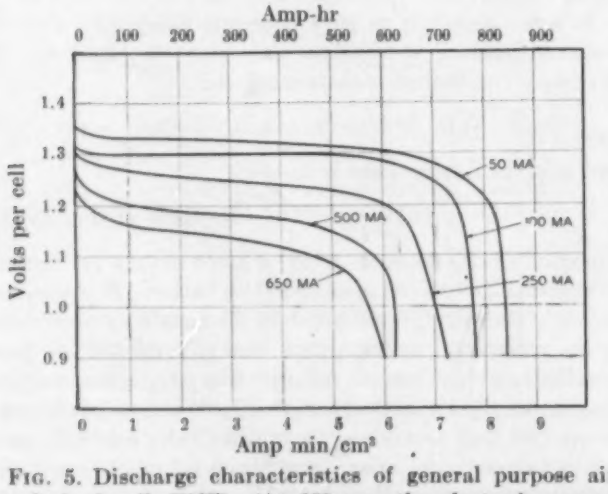

FIG. 5. Discharge characteristics of general purpose air-depolarized cell (70°F). (At 650 ma, the electrode current density is approximately 3.1 amp/ft² or 0.33 amp/dm².)

In consequence, carbon electrodes of a wide variety of shapes and configurations have been developed, these ranging from the conventional molded block to a cylinder or annulus (44) and various modifications of "ventilated" and hollow electrodes (45). In some cell types, the carbon has been used as the cell wall (46).

In a recently developed cathode, a layer of active carbon particles, bonded with a plastic, is attached directly to a perforated metal (e.g., iron) plate. An electrode of this type offers several advantages. It can be made much thinner than the conventional type and occupies less space; it is stronger; its conductivity is greater and depolarizing activity over the entire active surface is much more uniform.

The conventional cells are usually operated at current densities of 7 to 10 amp/ft² and higher drains are possible. With oxygen instead of air (47) well over 100 amp/ft² may be obtained.

Of the many cell forms that have been developed, the following are of greatest technical and commercial importance.

The simplest form of the air-depolarized cell, the "Railway" unit (Fig. 4), is designed, like its Lalande prototype, for final assembly in the field. Its component parts, a zinc:carbon electrode unit, granular caustic alkali, and oil, are separately packed and shipped dry. The emergent portion of the cathode is shielded by a plastic or metal collar (48) to protect the carbon from the oil layer.

Cells of this type are usually of 500 amp-hr capacity, capable of operating at drains as high as 2.0 amp on continuous, or 3.0 amp on intermittent load. Their rate of deterioration is slight so that their rated capacity can be realized over a service period of two years. Caustic soda electrolyte is generally satisfactory for temperatures down to 0°C or a little less (25°F); with caustic potash, cells remain operable at temperatures at least as low as −35°C (−30°F).

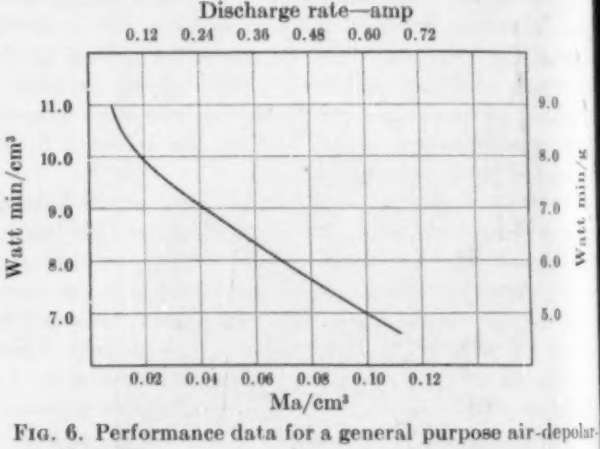

FIG. 6. Performance data for a general purpose air-depolarized cell (70°F).

Fully-assembled reserve cells of the water-activated type have also been made available (49), usually in units of 300–800 amp-hr capacity. These are generally characterized by a lower current output than the "Railway" cell, but provide a greater amp-hr capacity per unit of volume or weight than the latter (Fig. 5–6). One of the most common of these is shown in Fig. 7.

The battery, either in the form of a single cell or as two cells in series, is built into and enclosed in a plastic case. The electrode assembly is surrounded by cast sodium hydroxide monohydrate (50) ($NaOH \cdot H_2O$, mp 65°C), which protects the fragile carbon electrode from breakage during shipment and handling. Hydrated lime (51) compounded with cellulose floc or other extender (52) is placed at the bottom of the cell. This material reacts with dissolved zinc forming insoluble calcium zincate and thus regenerating exhausted electrolyte:

$$Ca(OH)_2 + Na_2Zn_2O_3 \rightarrow CaZn_2O_3 + 2NaOH. \quad (X)$$

The use of lime has made possible a reduction in electrolyte volume from an original requirement of 7–9 cc down to 3 cc per amp-hr.

The battery leaves the factory completely assembled and sealed to prevent deterioration. Activation is accomplished by breaking a frangible diaphragm (53) in the filler opening, adding tap water, and removing the seal (54) over the carbon.

[9] Weisz and Jaffe (36) believe that the conventional electrodes are sufficiently porous to permit diffusion of all the oxygen required for ordinary current loads.

Although considerable work has been done on the immobilization of caustic alkali electrolyte (55) only miniature air-depolarized dry cells have thus far been produced commercially. A cell (56) of 5.5 amp-hr (6.0 watt-hr) capacity, designed for use as "A" supply for portable hearing-aid sets is shown in Fig. 8.

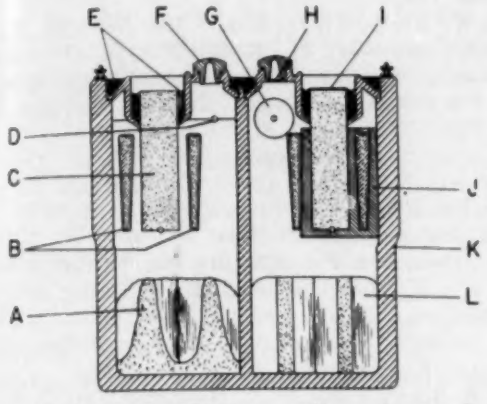

FIG. 7. Air-depolarized battery, radio, and general purpose type. Right: sealed cell, before water addition; left: activated cell ready for use. A—lime slurry; B—zinc anodes; C—carbon cathode; D—solution level indicator; E—asphalt seal; F—filler opening cap; G—auxiliary casting of $NaOH \cdot H_2O$ and $Ca(OH)_2$; H—frangible diaphragm; I—removable cellophane seal; J—cast caustic soda ($NaOH \cdot H_2O$); K—plastic case; L—briquetted lime.

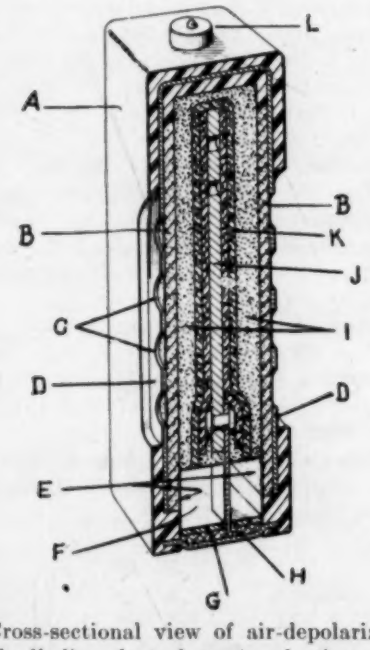

FIG. 8. Cross-sectional view of air-depolarized miniature dry cell with alkaline electrolyte. A—plastic case; B—carbon cathodes; C—ventilating apertures; D—metal support for cathode; E—carbon; F—air space; G—inner seal; H—negative terminal; I—electrolyte; J—zinc anode; K—paste support; L—positive terminal.

The unit, completely assembled at the factory, consists essentially of two metal-backed, plastic-bonded carbon cathodes (the metal perforated to permit air access) molded directly into a plastic container; an amalgamated, centrally located zinc anode; and a starch-gelatinized electrolyte of 9*N* caustic soda containing dissolved zinc.[10] In electrolyte of this composition the over-all cell reaction becomes

$$2Zn + O_2 \rightarrow 2ZnO. \qquad (XI)$$

The zinc oxide, precipitated in porous form, interferes very little with cell operation. The electrolyte is therefore substantially nonvariant, and no addition of lime is required to achieve high output. The cells, individually taped and packed in air-tight containers to prevent zinc corrosion and moisture loss, show little deterioration during shipment and storage. Once activated—by removal of tape—they should be placed in service as soon as possible and used under conditions in which their rated capacity can be delivered within about three to four weeks.

This cell is designed for comparatively low drains—30 to 60 ma (2 to 4 amp/ft² of electrode area)—and does not operate effectively at temperatures much below 15° to 18°C. Within its field of usefulness, however, it is probably the most efficient, per unit of weight (200 watt hr/kg) of the commercially available batteries.

* * *

The progress of the alkaline battery during the past fifty years has been spectacular. Its technical development (see Fig. 9) has been marked by a six- to sevenfold increase in electrical output per unit of weight or volume and its capabilities have by no means been exhausted. While interest in primary batteries continues, the importance of the alkaline cell should increase rather than diminish.

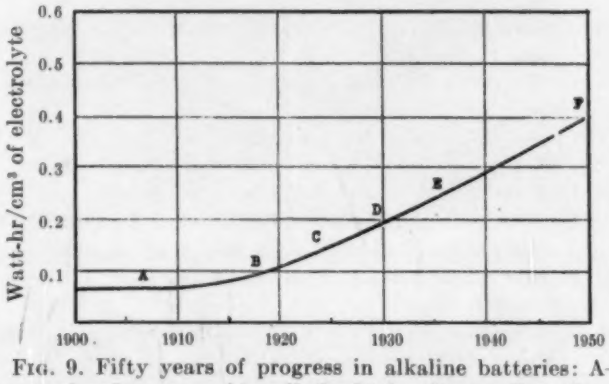

FIG. 9. Fifty years of progress in alkaline batteries: A—conventional copper oxide cell; B—high voltage cell (sulfured CuO); C—electrolyte regeneration (lime reactant); D—air depolarization (lime reactant); E—air depolarization (lime with extender); F—dry type, air-depolarized cell.

REFERENCES

1. A. DE LA RIVE, *Arch de l'Électricité*, **3**, 112 (1843).
2. F. DE LALANDE AND G. CHAPERON, French Pat. 143,644, June 25, 1881; German Pat. 22,702, June 28, 1882; U. S. Pat. 274,110 (1883); *Compt. rend.*, **97**, 164 (1883); **112**, 1243 (1891).
3. R. LORENZ, *Z. Elektrochem.*, **4**, 305, (1898).
4. A. J. ALLMAND AND H. J. T. ELLINGHAM, "Principles of Applied Electrochemistry," p. 211, Longmans, Green & Co., New York (1924).
5. ANON., *Elektrotech. Z.*, **11**, 377 (1890); **13**, 476 (1892); **21**, 205 (1900).
6. M. L. MARTUS, *Trans. Electrochem. Soc.*, **53**, 183 (1928); **68**, 151 (1935).
7. J. M. SPANGLER, *Proc. Am. Ry. Assn. (Signal Div.)*, **16**, 428 (1919).
8. C. FÉRY, *Electrician*, **80**, 320 (1917) from *C. A.*, **12**, 565 (1918); idem. *Compt. rend.*, **172**, 317–20 (1920); A. NASARISCHWILY, *Z. Elektrochem.*, **29**, 320–3 (1923).

[10] Addition of zinc oxide or hydroxide to alkaline electrolyte has long been practiced in the alkaline battery art (Desmazure, 1886; Boettcher, 1890) (57).

9. E. W. Jungner, British Pat. 145,018, June 12, 1920; H. D. Nyberg, *Z. Elektrochem.*, **30**, 549–52 (1924); S. Naray-Szabo, *Z. Elektrochem.*, **33**, 15–20 (1927); G. W. Heise and E. A. Schumacher, *Trans. Electrochem. Soc.*, **62**, 383–91 (1932); R. Ziegenberg, *Elektrotech. Z.*, 131–2 (1933).
10. A. Hantzsch, *Z. anorg. Chem.*, **30**, 298 (1902); F. Foerster and O. Günther, *Z. Elektrochem.*, **6**, 301 (1899); F. Goudriann, *Rec. trav. chim.*, **39**, 505, (1902); J. H. Hildebrand and W. G. Bowers, *J. Am. Chem. Soc.*, **38**, 785 (1916); R. Z. Fricke, *Z. anorg. allg. Chem.*, **134**, 344 (1924); E. Müller, *Z. Elektrochem.*, **33**, 134–144 (1927); R. Scholder and G. Hendrich, *Z. anorg. Chem.*, **241**, 76–92 (1939).
11. G. W. Heise, E. A. Schumacher and C. R. Fisher, *Trans. Electrochem. Soc.*, **92**, 173 (1947).
12. O. Klein, *Z. anorg. Chem.*, **74**, 157 (1912); E. Müller, *Z. Elektrochem.*, **33**, 134 (1927); H. G. Dietrick and J. Johnston, *J. Am. Chem. Soc.*, **49**, 1419 (1927); R. Scholder and H. Weber, *Z. anorg. allg. Chem.*, **215**, 355–366 (1933).
13. W. McA. Johnson, *Trans. Electrochem. Soc.*, **1**, 187 (1902); A. J. Allmand, *J. Chem. Soc.*, **95**, 2151 (1909); **97**, 603 (1910).
14. W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York (1938).
15. Association American Railroads, Signal Section Specifications 87–39 (1939).
16. G. W. Vinal, "Primary Batteries," John Wiley & Sons, Inc., New York (1950).
17. F. Lalande and G. Chaperon, cf. ref. (2); E. L. Marshall, *Trans. Electrochem. Soc.*, **25**, 467 (1914).
18. F. J. Wolfe, U. S. Pat. 1,564,741, Dec. 8, 1925.
19. R. W. Erwin, U. S. Pat. 1,282,057, Oct. 22, 1918; G. W. Armstrong, U. S. Pat. 1,624,460, April 12, 1927.
20. R. Lorenz, ref. (3); A. J. Allmand and H. J. T. Ellingham, ref. (4).
21. T. A. Edison, U. S. Pats. 1,207,382, Dec. 5, 1916; 1,386,095, Aug. 2, 1921.
22. A. I. Eddy, U. S. Pat. 2,157,072, May 2, 1939.
23. A. I. Eddy, U. S. Pat. 2,189,463, Feb. 6, 1940.
24. M. L. Martus, E. H. Becker and C. B. Schoenmehl, U. S. Pat. 1,532,252, April 7, 1925.
25. R. W. Erwin, U. S. Pat. 1,295,459, Feb. 25, 1919.
26. O. Arendt, *Elektrotech. Z.*, **27**, 27 (1906); cf. W. R. Cooper (27) p. 181.
27. W. R. Cooper, "Primary Batteries," p. 182 ff., "The Electrician" Printing and Publishing Co., London (1916).
28. W. Walker and F. H. Wilkins, U. S. Pats. 524,229 and 524,291 (1894).
29. L. Maiche, British Pat. 1,940, Oct. 24, 1882; Pollak and Wehr, French Pat. 170,411, July 31, 1885; A. v. Welsbach, French Pat. 321,330, May 21, 1903; J. Braunschild and D. Chapiro, French Pat. 409,076, April 12, 1910.
30. K. Kordesch and A. Marko, *Oesterr. Chem. Ztg.*, **52**, 125–31 (1951).
31. A. I. Eddy and E. O. Jegge, U. S. Pat. 2,233,593, March 4, 1941.
32. J. Dewar, *Proc. Roy. Soc. (London)*, **74**, 127 (1904); T. F. E. Rhead and R. V. Wheeler, *J. Chem. Soc.*, **101**, 846 (1912); **103**, 461, 1210 (1913); H. R. Kruyt and G. S. de Kadt, *Kolloid Z.*, **47**, 44 (1929); R. F. Strickland-Constable, *Trans. Faraday Soc.*, **34**, 1074 (1938); P. H. Emmett, *Chem. Rev.*, **43**, 69–148 (1948).
33. S. Naray-Szabo, ref. (9); N. Schilow, Schatunowskaja and Tschmutow, *Z. phys. Chem.*, **148**, 23[illegible], **149**, 211; **151**, 31 (1930); A. Frumkin, *Kolloid Z.*, **51**, 123 (1930); L. Lepin, *Physik Z. Sowjetunion*, **4**, 282 (1933); A. King, *J. Chem. Soc.*, p. 1688 (1936); N. M. Winslow, *Trans. Electrochem. Soc.*, **92**, 411 (1947).
34. R. E. Jones and D. T. A. Townend, *J. chim. phys.*, 47, 348 (1950).
35. G. W. Heise, *Trans. Electrochem. Soc.*, **75**, 163 (1939); M. Janes, *ibid.*, **77**, 413, 424 (1940); E. A. Schumacher and G. W. Heise, U. S. Pat. 2,365,729, Dec. 26, 1944.
36. F. Fischer and W. Krönig, *Z. anorg. allg. chem.*, **135**, 1[illegible] (1924); E. Berl, U. S. Pat. 2,000,815, May 7, 1935; M. Janes, *Trans. Electrochem. Soc.*, **77**, 415 (1940); W. G. Berl, *ibid.*, **83**, 253 (1943); G. W. Heise, E. A. Schumacher, and C. R. Fisher, ref. (11); R. Weiss and S. Jaffe, *ibid.*, **93**, 128 (1948).
37. M. Janes, U. S. Pat. 2,390,591, Dec. 11, 1945; cf. (11).
38. J. Jumas, *Ann. chim. anal.*, **27**, 11 (1945); cf. C. A. 40, 3062.
39. W. Wisfeld, U. S. Pat. 2,190,817, Feb. 20, 1940; K. Bratler, *Z. Elektrochem.*, **54**, 81–8 (1950).
40. E. A. Schumacher, V. C. Hamister, and G. W. Heise, U. S. Pat. 2,010,608, Aug. 6, 1935; cf. C. Drotschmann, "Trockenbatterien," 3rd ed., p. 313 ff., Akad. Verlagsges. Becker and Erler, Kom. Ges. Leipzig (1945).
41. G. W. Heise and E. A. Schumacher, U. S. Pat. 2,213,429, Sept. 3, 1940.
42. E. W. Jungner, Ref. (9), also G. W. Heise and E. A. Schumacher, U. S. Pat. 2,017,280, Oct. 15, 1935.
43. G. W. Heise and E. A. Schumacher, cf. (9), p. 385.
44. H. G. Thompson, U. S. Pat. 2,044,923, June 23, 1936.
45. E. Fournier, French Pat. 636,664, Jan. 14, 1928; R. Oppenheim, U. S. Pat. 2,097,077, Oct. 26, 1936; E. A. Schumacher and G. W. Heise, U. S. Pat. 2,207,763, July 16, 1940; C. R. Fisher, G. W. Heise, and E. A. Schumacher, U. S. Pat. 2,572,918, Oct. 30, 1951.
46. H. D. Nyberg, *Z. Elektrochem.*, **30**, 549 (1924); G. W. Heise and E. A. Schumacher, U. S. Pat. 2,207,734, July 16, 1940.
47. M. Janes, *Trans. Electrochem. Soc.*, **77**, 411 (1940).
48. Ref. (44) also G. W. Heise, U. S. Pat. 2,065,893, Dec. 29, 1936.
49. Heise, Schumacher, and Fisher, ref. (36), also Anon., *Ry. Sig.*, p. 176, March 1937; p. 47, Jan. 1950.
50. G. W. Heise, U. S. Pat. 1,924,314, Aug. 20, 1933.
51. G. W. Heise, U. S. Pats. 1,835,867, Dec. 8, 1931; 1,864,652, June 28, 1932.
52. G. W. Heise and E. A. Schumacher, U. S. Pat. 2,180,955, Nov. 21, 1939; L. S. Dunham and E. O. Jegge, U. S. Pat. 2,450,472, March 15, 1947.
53. D. Domizi, U. S. Pat. 2,151,902.
54. G. W. Heise, U. S. Pat. 2,074,506.
55. A. P. Manchester, U. S. Pat. 1,137,226, April 27, 1915; C. Ortli, U. S. Pat. 1,610,310, Dec. 14, 1926; G. W. Heise and E. A. Schumacher, U. S. Pats. 1,615,839, Feb. 1, 1927; 2,180,839, Nov. 2, 1939; S. Ruben, U. S. Pat. 2,576,266, Nov. 27, 1951.
56. G. W. Vinal, "Primary Batteries," p. 226, John Wiley & Sons, Inc., New York (1950); P. A. Marsal and R. P. Fox, U. S. Pat. 2,597,116, May 20, 1952; E. A. Schumacher and P. S. Brooks, U. S. Pat. 2,597,117, May 20, 1952; E. A. Schumacher and R. J. Bennett, U. S. Pat. 2,597,119, May 20, 1952.
57. A. Treadwell, "The Storage Battery," pp. 103-105, The Macmillan Co., New York, (1906).

The Alkaline-Mercury Oxide Cell

James M. Booe[1]

These alkaline-mercury oxide cells, as commercially produced, are dry cells, employing a depolarizer of mercuric oxide, an immobilized electrolyte of potassium hydroxide containing a substantial amount of zincate, and an amalgamated zinc anode.

Historical

In 1884 Clarke (1) described a mercuric oxide liquid alkaline primary cell as did Bronsted (2) in 1915. During World War I attempts were made to produce mercuric oxide liquid alkaline cells.

The "RM"[2] cell, developed by Samuel Ruben[3] in the early part of World War II, utilized a cathode-depolarizer of mercuric oxide and finely divided graphite compressed into a hard pellet, an amalgamated zinc anode, and electrolyte of potassium hydroxide substantially saturated with zincate, the electrolyte being held in an absorbent spacer-barrier interposed between the two electrodes, the cell elements being housed under compression in an air-tight sealed steel case. The cell contained no free flowing electrolyte.

Ruben's work demonstrated the ability of his cell to withstand severe storage and operating conditions over extended periods of time. The Battery Branch of the U. S. Signal Corps recognized this and promptly sponsored the development and establishment of production for relatively large numbers of cells for military use.

By the end of the war, peak production of the RM cell was in excess of 1,000,000 cells per day. Production has since continued on a large scale both for military and civilian use. The cell as manufactured today is considerably improved over the cells first manufactured during the last war, although the fundamental features are retained.

A number of patents (3) were issued to Ruben covering his developments.

Applications

Mercuric oxide cells are characterized by their high ratio of energy to volume, long shelf life, uniform discharge potential, resistance to environmental conditions of corrosion, temperature and pressure, and are mechanically rugged and stable. Although these cells will operate at such elevated temperatures as 125°C (257°F), their performance at rather low temperatures is limited except at low rates of drain.

One of the important applications of cells of this system is in the construction of multicell military batteries. Other uses include alarm systems, radiation detection devices, portable test apparatus, and scientific and clinical laboratory instruments. The main application of mercuric oxide cells, however, is for the "A" supply of hearing aids. The rather uniform open circuit voltage of this system makes it applicable as secondary standards of potential where extreme precision is not required. Because of this characteristic the cells lend themselves as a source of potential for the grid elements of electron tubes.

[1] P. R. Mallory & Company, Inc., Indianapolis, Indiana.

[2] A contraction of Ruben-Mallory used by the Signal Corps to designate the battery.

[3] Ruben Laboratories, New Rochelle, New York.

Anodes

The anodes used in the alkaline-mercuric oxide cells may be in one of the following general forms:

1. Amalgamated zinc powder of a special grade amalgamated with about 10 per cent of mercury by weight is pressed into the desired shape, such as a pellet or cylinder, under a pressure of several tons per square inch (Fig. 2). A highly porous structure is developed with considerable subsurface activity during use. The maximum current-density rating is about 18.5 ma/cm² (120 ma/in.²) of apparent area.

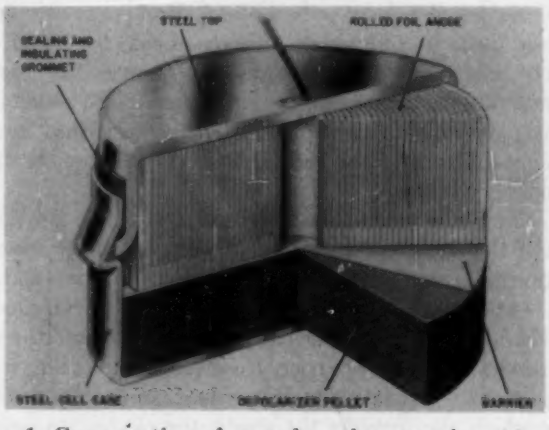

FIG. 1. Cross section of wound-anode mercuric oxide cell.

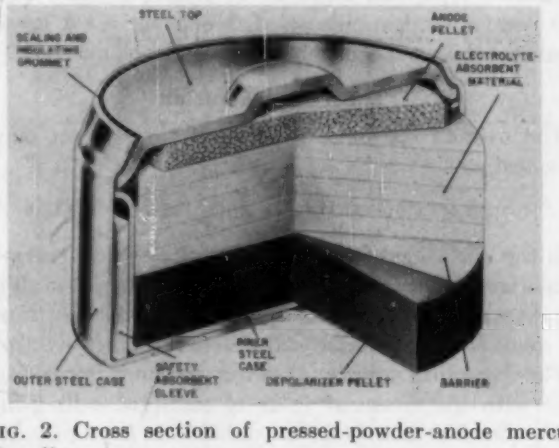

FIG. 2. Cross section of pressed-powder-anode mercuric oxide cell.

2. Corrugated zinc foil of 99.99 per cent purity is wound into a roll with an absorbent paper, the latter to retain electrolyte at the entire interface of the anode (Fig. 1). Winding is done in a staggered manner so that one edge of the zinc protrudes from one end of the roll and paper from the other. This type of anode is amalgamated, after saturation with electrolyte, by the addition of 10 per cent of metallic mercury to the end of the roll having the exposed edges of zinc.

3. Corrugated zinc foil or strip is wound into a roll without absorbent paper and, after transferring into the negative cell member, is amalgamated with metallic mercury.

This and other forms of wound anodes are used in cells with gelled electrolyte. Foil type anodes have a permissible current-density rating up to about 0.8 ma/cm² (5 ma/in.²).

Cathode

The depolarizer consists of an intimate mixture of about 92 per cent red mercuric oxide and 8 per cent micronized graphite, the latter imparting electronic conductivity. The mix is molded under high pressure directly into the cathode member (Fig. 1 and 2), or is pressed as a discrete part and assembled into the cell, depending on the type of cell produced. Permissible current-density rating of the cells based on depolarizer area is about 15.5 ma/cm² (100 ma/in.²).

Electrolyte

The electrolyte-separator members used in the alkaline-mercuric oxide cells are of two general types:

1. Liquid electrolyte of 35 to 40 per cent KOH content containing approximately 5 per cent ZnO is absorbed in a separator material of alpha cellulose. In wound-anode cells, a single layer of paper is used between the zinc windings, while in pressed-powder cells, multilayers of paper or cellulose felt are used. In addition to this absorbent, the liquid electrolyte cells require an ion-permeable "barrier" to prevent migration of particles from the depolarizer to the anode. This barrier, generally of parchment paper, is positioned next to the depolarizer interface, thus leaving the cellulose absorbent to contact the anode.

2. The other type of electrolyte-separator is a gelatinized form of the liquid electrolyte having approximately the composition indicated above. Gelling is effected by the addition of 1.5–4 per cent carboxy-methyl-cellulose. This can produce an electrolyte member sufficiently rigid to eliminate the need for paper absorbent or barrier. However, for the more severe applications a parchment barrier is used. In another arrangement which also involves the anode, the electrolyte-member is made by rigidly gelling a liquid electrolyte of approximately the same composition with carboxy-methyl-cellulose with the zinc powder amalgam dispersed throughout it.[4] A barrier is required between this member and the depolarizer.

Theory of Operation

The over-all discharge reaction of this system may be presented as:

$$Zn + HgO + H_2O \rightarrow ZnO + Hg + H_2O$$

with the liberation of two Faradays of electrical energy per mole of active electrode materials. In the above over-all reaction water appears on both sides of the equation; thus the net result is that no water is abstracted from the electrolyte.

The theoretical voltage (4) of this system is in close agreement with the measured value of stabilized cells, namely, 1.345 volts. The cells owe their stability, in large part, to the presence of potassium zincate in the electrolyte in substantially saturated concentration. This is produced in the preparation of the electrolyte by reacting ZnO with KOH.

$$ZnO + 2KOH \rightarrow K_2ZnO_2 + H_2O$$

The presence of the zincate ion inhibits the chemical attack of the KOH on the zinc anode by the mass action effect. In newly assembled cells an initial voltage of about 1.4 volts may be obtained. However, within a few hours the voltage becomes stabilized at or near the 1.345 value. Uniformity and stability is also promoted by the high degree of purity of all cell constituents.

In addition to the rather reproducible open-circuit voltage the system has a fairly constant discharge potential. Continuous-discharge capacity is virtually equal to intermitt discharge performance. These characteristics are prob due to the direct reduction of HgO to Hg without interm ate products, in combination with the fact that the elec lyte composition remains constant during discharge.

Cell Mechanics

The cell-discharge reactions are accompanied by defi physical changes in the electrodes and electrolyte-absorb member. Herein lies the necessity for a rather precise arra ment of these parts if optimum performance is to be reali In an undischarged cell with liquid electrolyte the anod supported in position by a moderate compression of the e trolyte-absorbent member against the cathode. In some electrolyte cells, the anode is loosely anchored in the negat terminal member as assembled; but during discharge, exp sion of the anode due to the formation of zinc oxide ex a slight but continuous compressive force on the gel-elect lyte member. The anode expands to about twice its origi volume during complete cell discharge. Mercury released the anode amalgam remains, in part, in the zinc oxide part accumulates on the negative terminal member. Provis must be made to prevent this free mercury from causing short circuit to the positive cell member. This is accomplish by an extension of the sealing gasket to the absorbent anode sleeve (Fig. 1 and 2). Also during discharge, the polarizer becomes soft due to its conversion to metallic m cury. Expansion of the anode tends to force electrolyte fr the absorbent or gel; this makes it available for absorption the depolarizer as the latter is progressively reduced. This important because reduction begins substantially at the su face and progresses through the depolarizer mass as the c is discharged.

Since the electrolyte is not consumed in the cell reaction a relatively small quantity is required, i.e., about 1.35 g/100 ma hr. Furthermore the energy–volume ratio of the electro material is quite high. Full advantage is generally taken these factors in the design of cells. This high energy–volum ratio is based on the fact that 1.00 g of HgO and 0.302 g zinc will produce 0.247 amp-hr of current. [Because of th graphite in the depolarizer and mercury in the anode, 1.00 of depolarizer (92% HgO, 8% graphite) and 0.308 g of anod amalgam (90% Zn, 10% Hg) will actually deliver 0.22 amp-hr.] At low rates of drain this amount of energy ca be realized, but at maximum rated drains somewhat less obtained, being as much as 10 to 15 per cent below the theo retical value, depending somewhat on the type of cell con struction. This performance is based on an end voltage of 0. volts.

The various factors of electrode reactions and their physica manifestations must be taken into account in the design an construction of the cell. This applies to the container as wel as to the active components. All cells are tightly sealed t prevent loss of electrolyte, to increase rigidity, and to avoid access of air to the active materials. All cells also have one external member, the negative terminal, forming part of the closure; this is generally termed the cell top (Fig. 1 and 2). This part is of material electrochemically suitable for contact with the anode in the presence of electrolyte. Among the ac ceptable metals are copper and certain of its alloys (preferably silver plated). Steel is preferred, although it requires a plat ing of an amalgamable metal such as tin. It is best also for the other external cell member and may be nickel plated to inhibit exterior cell corrosion. Steel has the property of inert ness to the alkaline electrolyte and to the depolarizer with which it must make good contact. This member serves as the

[4] Under development by The Magnavox Company, Fort Wayne, Indiana.

tive terminal for the cell and is generally termed the cell . Cells are tightly closed by deforming the edge of the tive member or case around the edge of the negative from ch it is insulated by a sealing gasket (Fig. 1 and 2). Ac- table gasket materials are polyethylene and neoprene, the er being used in cells for military applications or where ormal temperatures are encountered.

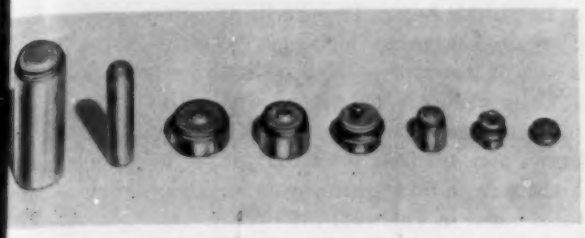

FIG. 3. Photographs of some mercuric oxide cells showing ative sizes and shapes. Identification (with Tables I and II) m left to right: RM-42 ("D" size), RM-502, RM-4, RM-3, RM-1, 1R, and RM-1RX.

TABLE I. *Dimensions and ratings of wound-anode mercuric oxide cells*

No.	Diam		Ht		Vol		Wt		Capacity
	(in.)	(cm)	(in.)	(cm)	(in.³)	(cm³)	(oz)	(g)	(ma hr)
1R	0.606	1.54	0.490	1.24	0.14	2.29	0.28	7.94	650
2R	0.819	2.08	0.518	1.32	0.27	4.42	0.56	15.9	1400
3R	0.973	2.47	0.523	1.33	0.38	6.23	0.84	23.8	2000
4R	1.187	3.01	0.541	1.37	0.60	9.85	1.30	36.8	3200

TABLE II. *Dimensions and ratings of pressed-powder-anode mercuric oxide cells*

No.	Diam		Ht		Vol		Wt		Capacity
	(in.)	(cm)	(in.)	(cm)	(in.³)	(cm³)	(oz)	(g)	(ma hr)
RM-1RX	0.606	1.54	0.226	0.574	0.070	1.150	0.14	3.97	250
RG-1	0.625	1.58	0.660	1.675	0.200	3.28	0.49	13.88	1000
RM-1	0.625	1.58	0.650	1.650	0.200	3.28	0.43	12.17	1000
RG-3	1.000	2.54	0.660	1.675	0.520	8.52	1.02	28.90	2000
RM-3	0.995	2.53	0.650	1.650	0.500	8.20	0.91	25.75	2000
RG-4	1.220	3.10	0.660	1.675	0.770	12.63	1.42	40.25	3400
RM-4	1.210	3.07	0.650	1.650	0.740	12.13	1.50	42.50	3200
RM-502	0.531	1.35	1.950	4.95	0.390	6.40	1.05	29.73	2400
RM-12	0.625	1.58	1.950	4.95	0.600	9.83	1.40	39.65	3600
RM-42	1.190	3.02	2.375	6.03	2.600	43.60	5.85	165.5	14000

RG is General Dry Battery Co. designation.
RM is P. R. Mallory & Co. designation.

The first cells produced were exclusively for military applications and were principally used in the construction of batteries for transceivers. A number of structural changes have since been made for civilian uses and for improved military service. The original negative-terminal zinc top was first replaced by copper and subsequently by tin-plated steel which is stronger, permits a more exact control of anode zinc content, and facilitates intercell welded connections. The acceptability of metals other than zinc for this cell part depends on a reaction in which the zincate ion in the electrolyte plays an important part. Upon assembly of the cell a local couple is established between the zinc anode and the cell top or terminal metal with which it is in contact. The potential of this couple is of sufficient magnitude to electrodeposit zinc from the electrolyte onto the terminal metal until it is completely covered; furthermore, this deposited zinc is amalgamated by mercury from the anode with which it is in contact.

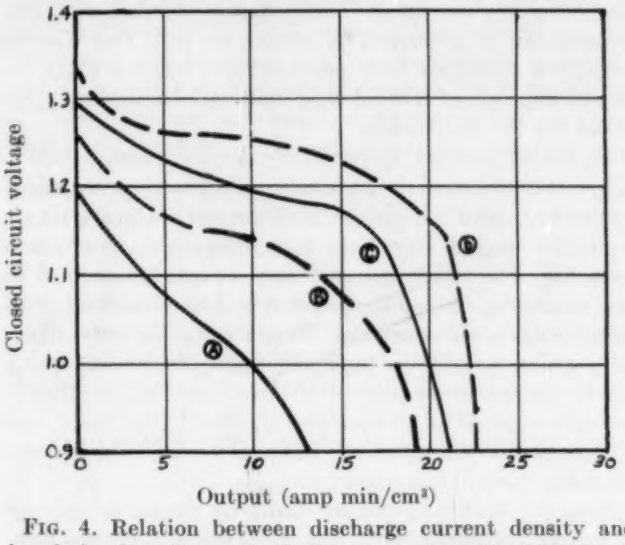

FIG. 4. Relation between discharge current density and closed-circuit voltage of alkaline-mercuric oxide RM-12 cell at 70°F.

Curve	Current density of discharge: Ma/in.² cathode area	Ma/cm² cathode area	Average ma/cm²	Average ma/in.²
A	122	18.9	25.4	417
B	61	9.45	12.7	208
C	30	4.65	6.3	103
D	15	2.32	3.0	50

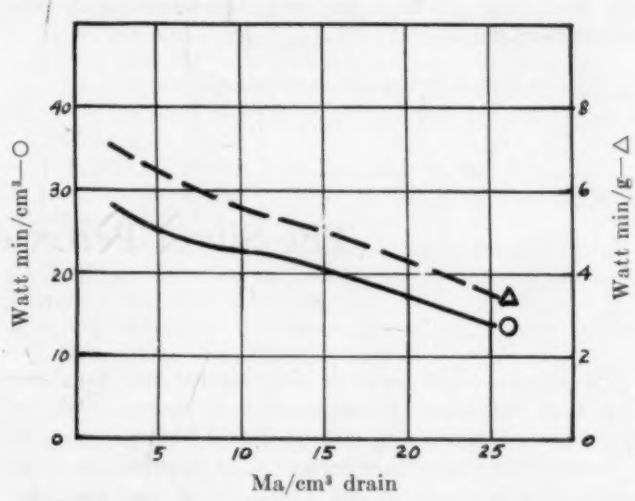

FIG. 5. Relation between discharge current density and output per unit volume and weight of alkaline-mercuric oxide RM-12 cell at 70°F to .9 v cutoff.

The position of the cell closure, originally at the top of the cell with resultant close spacing between the parts, has been somewhat changed. The radially-crimped cells (Fig. 1 and 2) which replaced the earlier axially-crimped cell, embodies a redesign of the cell exterior which extends the edge of the top member part way to the depolarizer and effects the seal at this point, thus increasing the distance between the anode and the positive member. This change, along with improved gasketing, has virtually eliminated the possibility of cell failures due to internal short circuits.

Another improvement in cell construction was effected for individual cell applications where the units are not enclosed in a battery container. When there is an electrochemical excess of anode zinc over the depolarizer, hydrogen gas is liberated at the cathode member after the depolarizer is spent if the cell is left on circuit. Under these conditions sufficient pressure can be developed to rupture the cell. This is overcome by a "balanced" (5) construction in which a slight excess of depolarizer is used over that stoichiometrically required for the zinc anode.

To further preclude the possibility of cell rupture from such causes as local action at the anode, unbalanced construction, externally applied voltage, etc., an improved venting[5] arrangement may be used. Essentially these cells are made with two cases, the outer effecting a seal with the cell top member in such manner as to hold the latter in sealing relationship with the top edge of the inner case. Should abnormal pressure develop within the cell, the top raises slightly to permit venting into the annular space between the two cases. Any electrolyte vented is retained by an absorbent member in this space, and any gas escapes through a hole in the outer case. Fig. 2 shows a cutaway view of this construction.

Some gel-electrolyte cells are vented by scoring the cell top to produce a weakened area. This gives way if abnormal pressures are generated, allowing gas and electrolyte to pass into a space between the top and an auxiliary terminal cap where any electrolyte is retained by an absorbent. Double case construction also is employed in gelled-electrolyte cells where venting takes place through the case rather than through the top.

Mercuric oxide cells, for the most part, differ in sizes and shapes from those of the Leclanché system. Fig. 3 shows some of the forms currently produced. (The largest cell shown is approximately the "D" size.) At present, cells of this system may be divided into three general groups according to their construction and uses.

[5] Subject matter for patent application.

1. Cells having a flat depolarizer element and a wound anode. Although these cells are generally unvented and unbalanced, some are made with these features. This type is primarily used for multicell battery constructions, especially for military applications. Table I lists such cells together with dimensions and ratings.

2. Cells having a flat depolarizer element and a flat pressed powder anode. (Gel cells with a wound corrugated zinc anode may be classed here.) These cells are vented and balanced and are used primarily for single cell applications. Table II lists cells of this type with their dimensions and ratings.

3. Cells having a cylindrical depolarizer element and a cylindrical pressed powder anode. These cells are vented and balanced and are used primarily for single cell applications and where drain rate requirements are high. Cells of this type are also found in Table II.

Performance of the alkaline-mercuric oxide system is represented in Fig. 4 and 5.

REFERENCES

1. C. L. Clarke, U. S. Pat. 298,175, May 6, 1884.
2. J. N. Bronsted, U. S. Pat. 1,219,074, March 13, 1917; British Pat. 16,474 (1915); German Pat. 72,147 (1916).
3. Samuel Ruben, U. S. Pat. 2,422,045-6, June 10, 1947; 2,473,546, June 21, 1949; 2,481,539, Sept. 13, 1949; 2,482,514, Sept. 20, 1949; 2,542,575-6, Feb. 20, 1951.
4. M. Friedman and C. E. McCauley, *Trans. Electrochem. Soc.*, **92**, 195 (1947).
5. S. Ruben, *Trans. Electrochem. Soc.*, **92**, 183 (1947).

References not specifically referred to in the text:

George W. Vinal, "Primary Batteries," John Wiley & Sons, Inc., New York, (1950).

R. W. Hallows and M. A. Cantab, "Dry Battery Developments—the RM Mercury Cell," *Wireless World*, May 1948.

John C. Lebens, "Portable Batteries for Built-in Power Sources," *Elec. Mfg.*, August 1949.

W. J. Hamer, "New Dry Cells," *Product Eng.*, March 1950.

C. H. Clark, "Primary Batteries," *Electrochem. Engrg.*, June 1950.

The Silver Peroxide-Zinc Alkaline Cell

Paul L. Howard[1]

The alkaline-silver peroxide-zinc element has been the subject of numerous investigations and patents. Only in recent years, however, has interest shifted from the study of its behavior as a secondary battery to an examination of its applicability as a primary cell. Clarke (1) in 1883 described a battery composed of silver oxide cathodes wrapped in vegetable parchment, bibulous paper, muslin or other suitable material, a zinc anode, and a sodium or potassium hydroxide electrolyte. Jirsa (2), Zimmerman (3), Kinoshita (4), and Andre (5) have described the use of silver oxide cathodes with anodes of iron, cadmium, or zinc. A list of the more important patents (6) by Jungner, Hubbell, Morrison, Brönsted, Drumm, Andre, and others shows how extensive the investigations have been in the secondary field.

The first practical silver peroxide-zinc alkaline reserve-type "one shot" high-rate primary battery was developed during World War II through the joint efforts of the National Bureau of Standards (7), the Naval Research Laboratory (8), and T. A. Edison, Inc., under the direction of the Bureau of Ships.

[1] National Bureau of Standards, Washington, D. C.

This battery is composed of a silver peroxide cathode consisting of a coating of silver oxide or silver chloride on a grid material such as silver-plated copper, nickel, or silver wire or screen, subsequently reduced to silver and electrolytically formed to silver peroxide (7), an anode of zinc consisting of sheet zinc, zinc plated or zinc dust pasted on copper, nickel or silver wire or screen, and an electrolyte of 25 to 35 per cent potassium hydroxide solution.

While the exact mechanisms of the electrode reactions (8) have not been completely established, the similarity of the changes taking place during discharge with those occurring in other alkaline cells suggests the following as the most probable mechanism (7):

$$Ag_2O_2 + 2\,KOH + Zn \rightarrow K_2ZnO_2 + H_2O + Ag_2O$$
$$Ag_2O + 2\,KOH + Zn \rightarrow K_2ZnO_2 + H_2O + 2\,Ag.$$

Denison (7), Vinal (8), and White, Pierce, and Dirkse (9) have outlined the performance characteristics of this system.

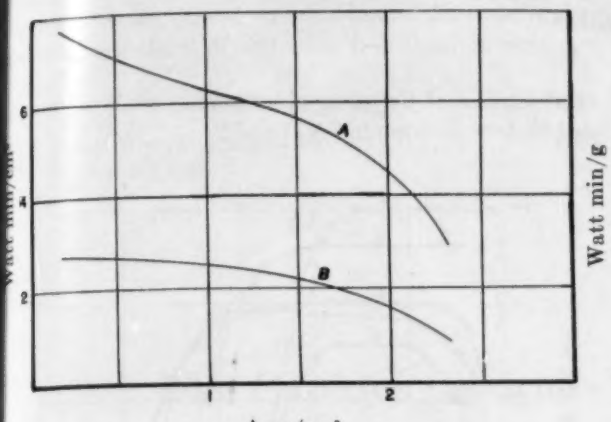

FIG. 1. Output per unit volume (A) and per unit weight (B) for silver peroxide-zinc cell.

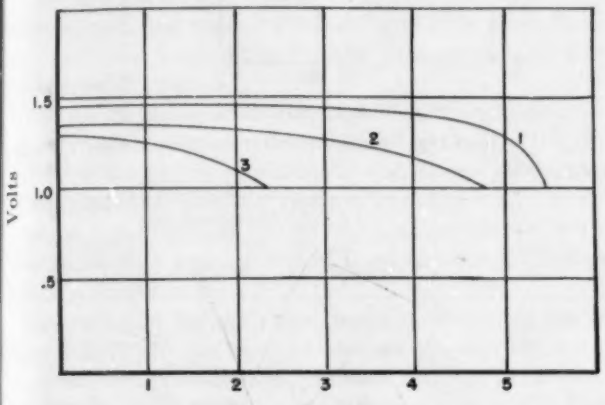

FIG. 2. Discharge characteristics for silver peroxide-zinc cell. Curve 1—0.19 amp/cm², electrode current density of 0.0357 amp/cm² (0.23 amp/in.²); curve 2—1.55 amp/cm², electrode current density of 0.233 amp/cm² (1.50 amp/in.²); curve 3—2.32 amp/cm², electrode current density of 0.349 amp/cm² (2.25 amp/in.²).

They have shown that it is suited for operation at temperatures above 0°C but not in excess of 85°C, for continuous discharge at current densities up to 1.0 amp/cm² (2.5 amp/in.²), throughout periods of from 1 minute to several hours, and for indefinite storage in the dry state but limited to 24 to 72 hours activated stand life prior to use.

The over-all performance of this battery has been compiled for a discharge condition where the batteries were discharged at a constant current to a 1.00 volt end point at a temperature of 27°C. Fig. 1 gives the watt minutes per cubic centimeter and per gram and Fig. 2 gives the variation in voltage for rates ranging from .19 amp/cm² to 2.32 amp/cm².

These batteries have not been developed for commercial production; however, experimental batteries have been made.

REFERENCES

1. C. L. CLARKE, British Pat. 1932, April 17, 1883.
2. F. JIRSA, *Z. Elektrochem.*, **33**, 129 (1927).
3. J. G. ZIMMERMAN, *Trans. Electrochem. Soc.*, **68**, 231 (1935).
4. K. KINOSHITA, *Bull. Chem. Soc., Japan*, **12**, 164, 366 (1937); **15**, 59 (1940); **15**, 82 (1940).
5. H. ANDRE, *Bull. soc. franç. elec.*, **1**, 132 (1941).
6. E. W. JUNGNER, German Pat. 110,210, Mar. 14, 1900; U. S. Pat. 670,024, Mar. 19, 1901; U. S. Pat. 692,298, Feb. 4, 1902.
   W. FAIRWEATHER, British Pat. 8365, Oct. 13, 1904.
   H. C. HUBBELL, U. S. Pat. 793,078, June 27, 1905; (to Portable Electric Safety Light Co.), U. S. Pat. 897,833, Sept. 1, 1908; British Pat. 17,331, Jan. 14, 1909.
   D. P. PERRY (to W. Morrison and M. A. Lumbard), U. S. Pat. 942,279, Dec. 7, 1909.
   W. MORRISON, U. S. Pat. 976,092, Nov. 15, 1910; British Pat. 18,360, July 11, 1912.
   J. N. BRÖNSTED, British Pat. 16,471, Sept. 7, 1916.
   F. P. HABICHT, British Pat. 152,364, Feb. 14, 1922.
   L. A. LEVY AND ALMEIDA ACCUM. LTD., British Pat. 298,289 (1927).
   J. J. DRUMM, British Pat. 335,587, Sept. 29, 1930; British Pat. 365,125, Jan. 18, 1932.
   P. ANTEBI, French Pat. 766,334, April 9, 1934.
   H. G. ANDRE, U. S. Pat. 2,317,711, April 27, 1943; U. S. Pat. 2,594,709 through 2,594,714, April 29, 1952; French Pat. 813,319, Feb. 22, 1937; 824,022, Nov. 3, 1937; 831,282, May 30, 1938; 926,470, April 21, 1947; 972,362, April 30, 1950.
   S. RUBEN, U. S. Pat. 2,422,045, June 10, 1947.
   I. A. DENISON AND P. L. HOWARD, U. S. Pat. 2,513,292, July 4, 1950.
7. I. A. DENISON, *Trans. Electrochem. Soc.*, **90**, 387, (1946).
8. G. W. VINAL, "Primary Batteries," p. 266, J. Wiley & Sons, Inc., New York (1950).
9. J. C. WHITE, R. T. PIERCE, AND T. P. DIRKSE, *Trans. Electrochem. Soc.*, **90**, 467 (1946).

Silver Chloride-Magnesium Reserve Battery

Ivan C. Blake[1]

Silver chloride-magnesium water-activated batteries first became available on a commercial basis in 1943. In the period of 1943–45, several battery types using silver chloride-magnesium water-activated cells were produced for the military. In the period of 1945–52, applications for these batteries became more numerous and batteries are now produced on a commercial basis for a diversified list of military and civilian uses.

The silver chloride-magnesium cell consists of an anode of unalloyed, high purity magnesium, a cathode system of silver and silver chloride, and an absorbent separator of cellulosic material. The cells are maintained in the inactive state by assembling the dry elements into cells or batteries in the absence of electrolyte and immediately packing the cells or batteries in hermetically sealed containers. At the time the cells or batteries are used, they are immersed in water to render them active. When the cell is discharged, the following reactions take place:

$$Mg \rightarrow Mg^{++} + 2e$$
$$2AgCl + 2e \rightarrow 2Cl^{-} + 2Ag$$
$$Mg^{++} + 2Cl^{-} \leftrightarrows MgCl_2 \cdot 6H_2O.$$

The reactions proceed with great rapidity and the cell develops its full voltage and current delivering power very rapidly. Inasmuch as the silver chloride is reduced to silver metal, the electronic conductivity of the depolarizer mass is increased as the discharge reactions proceed and the operating voltage of the cell is maintained at a high and constant value. When the silver chloride is completely reduced to silver metal, the voltage falls rapidly.

The operating voltage of cells and batteries ranges from 1.32 v per cell at a discharge current density of 2.00 amp/cm² (32.78 amp/in.²) or 0.072 amp/cm² to 1.60 volts per cell at a discharge current density of 0.006 amp/cm² (0.10 amp/in.²) or 0.0002 amp/cm².

Silver chloride-magnesium batteries, after activation in water at temperatures above O°C, can be discharged at ambient temperatures ranging from +94°C to −54°C, with outputs at either extreme of the temperature range being substantially the same as the output at +21°C.

Several variations of cell and battery designs are manufactured. A cell for discharge at extremely high current densities consists of an anode of thin magnesium sheet and a cathode of silver foil, upon the surfaces of which a layer of silver chloride has been electroformed, separated by a layer of thin absorbent paper. The cell components are rolled up to form a cylindrical cell having a large active surface area per unit of volume. Such cells are usually designed for discharges to be completed in 30 minutes or less.

Batteries for applications requiring lower current densities, longer life (0.5–24 hours), and a relatively constant discharge voltage are made from cells using flat depolarizer sheets of rolled silver chloride, magnesium sheet anodes, and relatively thick absorbent pads as separators.

Silver chloride-magnesium water-activated batteries are available in sizes ranging from 1 to 1050 ampere minutes rated capacity and in voltages ranging from 1.5–150.

[1] Burgess Battery Company, Freeport, Illinois.

Performance of the silver chloride-magnesium water-activated battery is shown in Fig. 1 and 2.

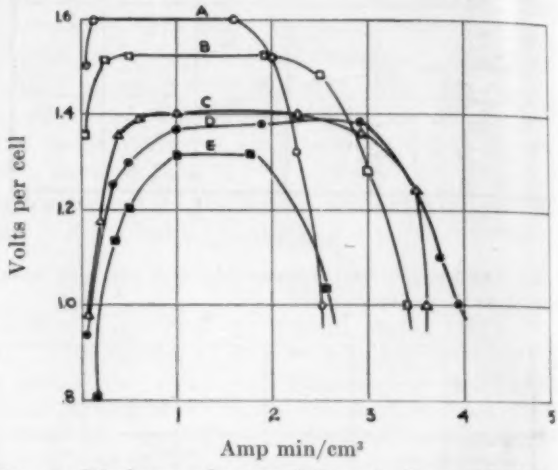

FIG. 1. Discharge characteristics of silver chloride-magnesium cell.

Curve	Discharge current		
	Amp/cm²	Amp/in.²	Amp/cm² of electrode area
A	0.006	0.098	0.0002
B	0.100	1.639	0.0034
C	0.500	8.195	0.0180
D	1.000	16.390	0.0360
E	2.000	32.780	0.0720

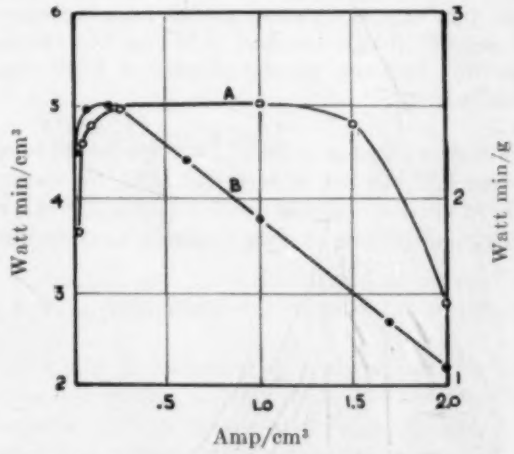

FIG. 2. Output per unit of volume (A) and weight (B) for the silver chloride-magnesium cell.

These batteries are used in airborne electronic equipment, signal lights, emergency flares, lights for pilot balloons, marker lights for floating buoys, light units for movie work, d-c motors, Radiosonde units for weather observation work, emergency radio equipment, air-sea rescue equipment, ignition systems, emergency lights for hospitals, and direction finding equipment.

Silver chloride-magnesium water-activated batteries are characterized by high current and power output, constant

potential, light weight, long shelf life in the inactivated condition, and are capable of being discharged at temperatures ranging from +94°C to −54°C. They have the disadvantages of being relatively high in cost (because of the silver content) and of inconvenience of activation procedures in certain applications.

REFERENCES

1. H. E. Lawson (To Burgess Battery Co.), U. S. Pat. 2,428,850, Oct. 14, 1947.
2. H. E. Lawson (To U. S. A.), U. S. Pat. 2,445,306, July 13, 1948.
3. J. B. Mullen (To Burgess Battery Co.), U. S. Pat. 2,521,082, Sept. 5, 1950.
4. L. H. Harriss (To Burgess Battery Co.), U. S. Pat. 2,543,106, Feb. 27, 1951.
5. J. B. Mullen and P. L. Howard, *Trans. Electrochem. Soc.*, **90**, 529 (1946).
6. G. W. Vinal, "Primary Batteries," pp. 274–279, John Wiley & Sons, Inc., New York, N. Y. (1950).

The Cuprous Chloride-Magnesium Reserve Battery

L. E. Pucher[1]

Cuprous chloride-magnesium, water-activated reserve-type batteries were first made commercially in 1949, these having been developed particularly for the military. Several types are now being produced.

The use of cuprous chloride as the oxidizing agent in a primary pile-type battery was suggested as early as 1891 in a British patent (1), in combination with a zinc anode and a 40 per cent zinc chloride electrolyte. Adams (2) in 1943 patented a reserve-type cell having a magnesium cylindrical can anode with a cathode core of fused cuprous chloride cast around a copper core.

The cells and batteries now being made are of the pile type. A sheet of magnesium of at least commercial purity is separated from the cuprous chloride cathode by a porous separator made of various natural or synthetic textile fibers. This separator also serves to retain the aqueous activating liquid. The cathode is preferably of the pasted type which activates much more rapidly than the fused type. It is made by applying a paste of powdered cuprous chloride and a liquid binder onto a suitable base, such as a grid of copper or bronze screen, though copper foil may be used. A suitable binder is polystyrene dissolved in an organic solvent such as toluol. Aqueous salt solutions also may be used as binders.

The battery of assembled cells is taped together under pressure. Uniform pressure and separator spacing throughout the assembled battery is essential for efficient operation. Because cuprous chloride is hygroscopic, assembled cells and batteries must be stored in dry sealed containers until activated to prevent the formation of cupric chloride. Absorbed moisture lowers the discharge voltage markedly and decreases the output.

During discharge the following reaction occurs:

$$Cu_2Cl_2 + Mg + CH_2O \rightarrow 2Cu + MgCl_2 \cdot CH_2O.$$

The performance of a representative cuprous chloride-magnesium, water-activated battery is shown in Fig. 1. A short voltage build-up time of 1 to 10 minutes is required after activation but this does not result in appreciable self-discharge. However, the cell should be used immediately after this voltage build-up. The open-circuit voltage varies with test conditions, rising to a maximum of 1.70 to 1.80 at 22°C (72°F). Because the discharge reaction proceeds rapidly the cell voltage is maintained at a high value until the cell is exhausted as shown in Fig. 1. The formation of $MgCl_2 \cdot 6H_2O$ tends to block the cell because its combined water is obtained at the expense of the water added to activate the cell.

This couple is best suited to discharges at low current densities, for example, 0.0065 to 0.049 amp/cm² (0.027 to 0.318 amp/in.²) of anode surface in cells having a volume of 1.64 to 3.88 cm³ (0.107 to 0.236 in.³). The discharge reaction is sufficiently exothermic to cause overheating on high current drains. This characteristic can be utilized to advantage in cells which must be operated in extremely low temperatures,

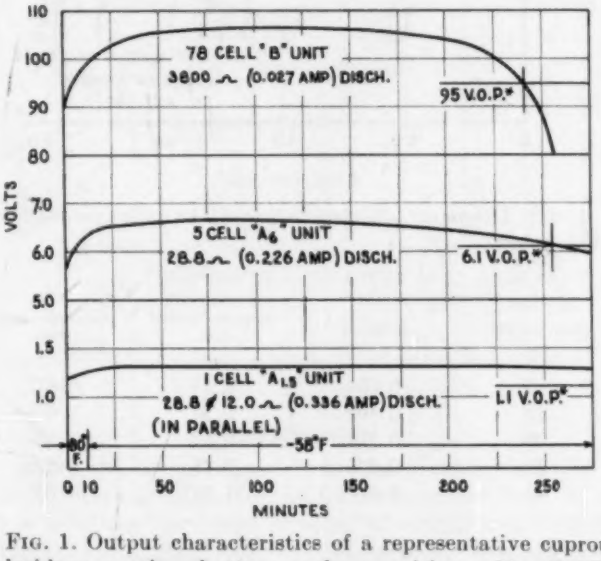

FIG. 1. Output characteristics of a representative cuprous chloride-magnesium battery pack comprising a 78 cell "B" unit discharged on 3800 ohm, a 5 cell "A" unit discharged on 28.8 ohm and an additional load on one "A" cell (bottom curve).

Curve	Amp	Min service	Amp cm³	Volts	Amp min cm³	Watt min cm³
Top	0.027	240	0.010	1.34	2.39	3.19
Middle	0.226	255	0.016	1.31	3.93	5.13

for example, at −50°C (−58°F) after activating at room temperature. Under these conditions the discharge characteristics are similar to those obtained at room temperatures (Fig. 1). The discharge efficiency is relatively low, probably of the order of 50 per cent.

[1] The Willard Storage Battery Company, Cleveland, Ohio.

Cuprous chloride-magnesium batteries are characterized by good current and power-output, almost constant potential, long shelf life, and are capable of being discharged in temperatures as low as −50°C after being activated at room temperature. They have a considerable cost advantage over the silver chloride-magnesium cells which have similar characteristics. However, the cuprous chloride cell is slightly heavier per unit of output.

REFERENCES

1. Walter Wensky British Pat. 49, 1891.
2. B. N. Adams, U. S. Pat. 2,322,210, June 22, 1943.

The Lead Dioxide-Cadmium Reserve-Type Cell

L. E. Pucher[1]

Although cadmium has long been recognized (1, 2) as a potential anode material, the limited storageability of the cadmium-lead peroxide cell prevented the general commercialization of this system. However, the demand for special purpose battery units, where storageability was of minor importance, provided the impetus for the development of this battery (3).

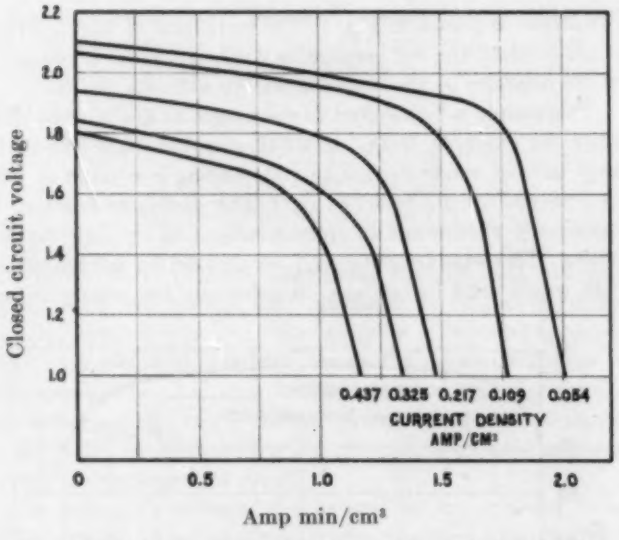

Fig. 1. Discharge characteristics of the cadmium-lead peroxide primary cell.

Current drain in amperes

Amp per cell	Amp/cm²	Amp/in.² anode area	Amp/cm² anode area
5	0.054	0.13	0.837
10	0.109	0.26	1.675
20	0.217	0.52	3.350
30	0.325	0.78	5.020
40	0.437	1.04	6.705

The reaction, similar to that of the Pb-PbO_2 couple in the lead-acid storage battery, follows:

$$PbO_2 + Cd + 2H_2SO_4 \rightarrow PbSO_4 + CdSO_4 + 2H_2O.$$

The positive plates are of the lead-acid type, pasted in the usual lead-antimony grid and formed in the conventional manner against lead cathodes. Special effort is made to achieve a highly peroxidized PbO_2 to ensure maximum capacity. While the positive grids formed in this manner are preferred, some work has been done with lead-plated copper screen as the positive grid. The results compare favorably with those obtained with the conventional type. Using copper-screen grids, considerable reduction in battery weight can be realized, but it is essential that the lead plating on the grids be sufficiently thick and nonporous to withstand mechanical abrasion during pasting and to resist penetration by the electrolyte.

Negative plates consist mainly of lead-plated copper-screen grids pasted with CdO-water mixes and electroformed to sponge cadmium. Electro-deposited and sheet cadmium have also been tried as negatives. For 26.7°C (80°F) operation at relatively low discharge rates, corrugated and perforated cadmium sheet can be used, but for high-rate discharges and lower-temperature operation, the sheet cadmium is unsatisfactory. Cadmium-sponge negatives are more promising.

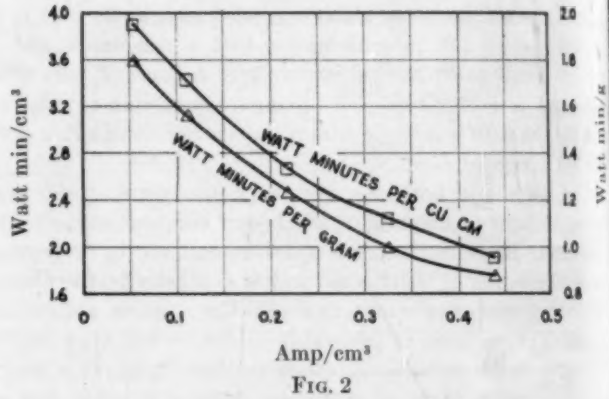

Fig. 2

TABLE I. *Effect of cell temperature on capacity of cadmium-lead peroxide cells*

amp min/g of wet cell weight

Temperature	Discharge rates					
	5 amp	10 amp	15 amp	20 amp	30 amp	40 amp
26.7°C (80°F)	0.91	0.81	0.68	0.68	0.62	0.54
4.4°C (40°F)	0.83	0.75	0.59			
−17.8°C (0°F)	0.79	0.64	0.49			
−28.9°C (−20°F)	0.47	0.45	0.39			

Various special papers such as Aldex[2] and Viskon[3], and fibrous materials such as Fibrite[4], Webril[5], and microporous rubber sheet have been used as separators between the plates.

An aqueous sulfuric acid solution with a specific gravity of 1.300 (39.5% H_2SO_4) is used as electrolyte.

The battery used for the plotted data in Fig. 1 and 2 had the following specifications:

Outside dimensions—3.25 x 4.68 x 6.03 cm (1 9/32 x 1 13/16 x 2 3/8 in.).

[1] The Willard Storage Battery Company, Cleveland, Ohio.

[2] Manufactured by Aldine Paper Products Company.
[3] Manufactured by The Visking Corporation.
[4] Manufactured by Willard Storage Battery Company.
[5] Manufactured by Kendall Mills.

Inside dimensions—2.78 x 4.22 x 5.57 cm ($1\frac{3}{32}$ x $1\frac{11}{16}$ x $2\frac{3}{16}$ in.).

Plate size—3.82 cm² (1¼ in.²), 0.1016 cm (0.040 in.) thick for the positive and 0.0762 cm (0.030 in.) thick for the negative. The battery consisted of seven pasted lead-antimony grid positives and eight plated copper-screen negatives covered with sponge cadmium. Open-circuit voltage is approximately 2.4.

The batteries were discharged at the constant current density shown in Fig. 1. The performance characteristics are shown in Fig. 1 and 2.

Table I shows the capacity of a representative cadmium-lead peroxide cell at various discharge rates and at temperatures of −28.9°C (−20°F) to +26.7°C (80°F). Lower discharge voltages and lower capacities result when batteries are dry-stored for extended periods.

The sponge-cadmium cells have a slightly higher discharge voltage and a slightly greater capacity than the lead-lead peroxide cells at higher discharge rates and at lower temperatures. They also are lighter in weight.

This system has been adapted to special military-purpose units where high drain and light weight are important factors. These units must be used promptly after activation since sponge cadmium plates react vigorously with the sulfuric acid electrolyte, with liberation of hydrogen. Open-circuit stands of more than one hour after activation are not recommended. The vigorous gassing also presents a serious problem in the design of nonspill or sealed units.

REFERENCES

1. V. M. Harris, U. S. Pat. 581,283, April 27, 1897.
2. E. Commelin, British Pat. 6619, March 18, 1904.
3. A. Fischbach, *Elec. Eng.*, p. 703 August (1950).

The Lead Dioxide-Zinc Reserve-Type Cell

W. J. Schlotter[1]

The lead peroxide-zinc couple has been recognized for years as possessing several features which make it attractive for primary battery use, mainly low cost and high voltage. Although this couple had been investigated from time to time since 1843 (1), no practical use was made of it because of its erratic behavior due to negative polarization effects, high gas evolution, and poor shelf life. From 1941 to 1949, The Electric Storage Battery Company carried on an intensive research and development program to perfect this couple as a reserve-type battery for military use. The objectives set forth during this period were met and over 200 full-size experimental batteries having outputs as high as 90 kilowatts were delivered for test. The information presented in this article is based on this work which includes tests on well over 3000 individual cells.

Because of the reactiveness of zinc in sulfuric acid, accompanied by the evolution of hydrogen gas, it is necessary to store this cell in a dry condition and to introduce the electrolyte when the cell is put into use. This may be accomplished by means of a self-contained chamber electrically or mechanically operated, or the electrolyte may be introduced from an external source.

The negative plate consists of a thin, rolled sheet of chemically pure zinc alloyed with mercury. This purity is necessary to prevent excessive gas evolution during operation. The surface is prepared by degreasing, followed by etching in hydrochloric acid. Performance of the negative plate is greatly dependent upon the alloying and surface preparation processes used.

The positive plate consists of a lead-alloy grid filled with lead peroxide and is very similar in construction and composition to the positive plates used in lead-acid storage batteries. Composition of the lead alloy used in the grid greatly determines the shelf life of the unactivated cell, while the method of preparing the lead peroxide influences the initial capacity of the cell. Advances in recent years in the preparation of storage-battery plates have been used to advantage in preparing positive plates for this couple.

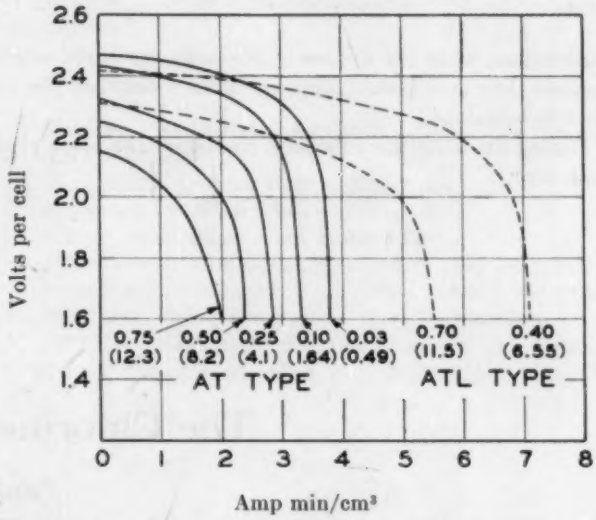

FIG. 1. Discharge characteristics for PbO_2-Zn reserve-type cell. AT type in solid lines, ATL type in broken lines. In AT type to convert amp/cm² to amp/cm² multiply by 0.319 (to amp/in.² multiply by 2.06). In ATL type to convert amp/cm² to amp/cm² multiply by 0.218 (to amp/in.² multiply by 1.41).

Curves left to right—discharges at

0.75 amp/cm² = 12.3 amp/in.²
0.50 amp/cm² = 8.2 amp/in.²
0.25 amp/cm² = 4.1 amp/in.²
0.10 amp/cm² = 1.64 amp/in.²
0.03 amp/cm² = 0.49 amp/in.²
broken lines
0.70 amp/cm² = 11.5 amp/in.²
0.40 amp/cm² = 6.55 amp/in.²

Although numerous types of separators may be used, all must have a low resistance and must provide a free path for the escape of gas from the negative plate. Woven plastic

[1] The Electric Storage Battery Company, Philadelphia Pennsylvania.

screen and porous paper have been used to advantage. The internal cell construction determines the type to be used.

The electrolyte is chemically pure sulfuric acid ranging in concentration up to 50 per cent. Concentrations below 35 per cent are rarely used. The concentration selected depends on the end use of the cell. Higher concentrations produce high positive plate efficiencies but increase negative plate

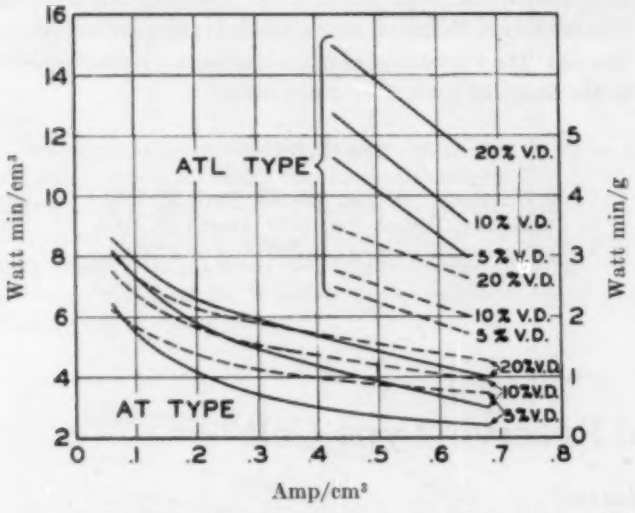

FIG. 2. Output per unit volume in solid lines, and per unit weight in broken lines to end points of 5%, 10%, and 20% below initial closed-circuit voltage for PbO_2-Zn reserve-type battery. (——, watt min/cm³; - - - -, watt min/g; V.D., voltage drop.)

polarization, while the reverse is true with the lower concentrations. For maximum output, a balance between the two must be obtained.

During discharge the following reactions take place at the electrodes:

$$Zn \rightarrow Zn^{++} + 2e$$
$$Pb^{++++} \rightarrow Pb^{++} - 2e.$$

If the reaction products are allowed to accumulate and block off unreacted portions of the electrodes, polarization occurs. At the negative electrode the reaction product is soluble and is removed by natural circulation of the electrolyte due to temperature differentials and evolved gas. Since the cathode reaction product is insoluble, the positive plate must be of such porosity that the reaction product does not block off the unreacted portion.

This couple is extremely sensitive to temperature. For any given set of cell conditions such as discharge current density, electrolyte concentration, etc., there is a minimum operating temperature. If the cell is operated below this minimum temperature, the cell output is only a small fraction of that obtained at the proper temperature. This falling off of output with temperature is due to polarization effects at the negative electrode. The minimum operating temperature is generally quite high, for example, the ATL type shown in Fig. 1 and 2 has a minimum operating temperature of 32°C (90°F) at the rates shown. At these same rates the AT type can be operated at 27°C (80°F).

The accompanying curves indicate the capacity output of two types of this cell, differing both in internal construction and concentration of electrolyte. The AT type uses 37 per cent sulfuric acid while the ATL type uses 50 per cent sulfuric acid and has very high output but is suitable for use over only a narrow range of current densities due to polarization effects at the negative electrode.

The following advantages can be realized from this couple: (*a*) high voltage, (*b*) capable of operating at moderately high current densities, (*c*) good shelf life in dry condition, and (*d*) low cost.

The following disadvantages are inherent in the operation of this couple: (*a*) high gas evolution and (*b*) poor low temperature characteristics.

REFERENCE

1. G. W. VINAL, "Primary Batteries," p. 302, John Wiley & Sons, Inc., New York (1950).

The Chlorine-Zinc Primary Cell

Paul L. Howard[1]

Many attempts have been made to utilize the halogens as depolarizers in primary batteries. Tomassi (1) describes a chlorine-depolarized cell as a "Pile De Le Roux" (1853). This was composed of a carbon cathode, a zinc anode, and a solution of hydrochloric acid as the electrolyte. Manganese dioxide was used as the reactant to supply the chlorine to the cathode. Zenger (2) patented the use of halogens as depolarizers for both primary and secondary batteries. In the past the main emphasis was placed on the use of halogens in secondary batteries (3–7) with no great measure of success. The first practical chlorine-depolarized primary cell was described by Heise, Schumacher, and Cahoon (8).

This chlorine-depolarized cell is a flat unit composed of a porous carbon layer for the diffusion of chlorine gas to be absorbed by a cathode cake of carbon black moistened with a 10 per cent zinc chloride solution, a separator consisting of a bibulous material impregnated with a methyl-cellulose gel (8), and anodes of zinc, aluminum, or magnesium. The inactive side of the anode is provided with an inert conducting coating to make a dry contact with the porous carbon of the next cell in series.

The chlorine gas is absorbed in the moist carbon black cake to act as the depolarizer. The cathode, anode, and complete cell reactions are, respectively:

$$Cl_2 + 2e \rightarrow 2Cl^-$$
$$Zn \rightarrow Zn^{++} + 2e$$
$$Cl_2 + Zn \rightarrow ZnCl_2.$$

Other anodes substituted for zinc give the corresponding cell reactions. The open-circuit voltage of cells using these anodes is 2.1 v with zinc, 2.4 v with aluminum, and 2.8 v with mag-

[1] National Bureau of Standards, Washington, D. C.

nesium. The aluminum and magnesium anodes are not considered in applications requiring extended inactive shelf life.

It is essential that the carbon black cake and separator maintain the proper moisture content throughout cell manufacture, assembly into batteries, and inactive shelf life. This is accomplished by sealing the finished assembly of cells into a container capable of withstanding internal pressures of 150 psi,[2] with a hygroscopic salt present to maintain the moisture content in the cells.

When the battery is being prepared for use, it is evacuated, sealed, and the liquid chlorine supply attached. At the time

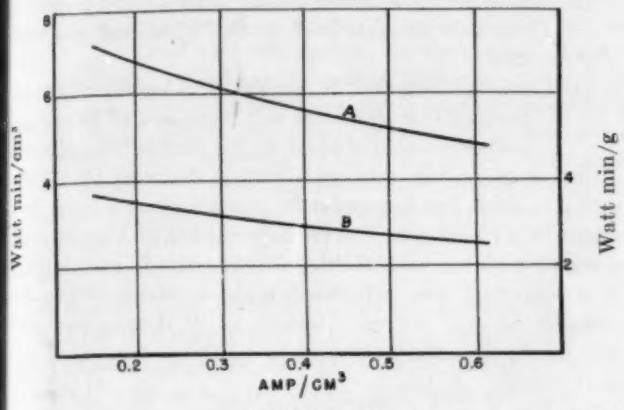

FIG. 1. Output per unit volume (A) and per unit weight (B) for chlorine-zinc cell.

of use, the liquid chlorine is admitted to the battery. It vaporizes immediately to give a partial pressure of chlorine gas corresponding to the battery temperature. A temperature of at least 20°C should be maintained to give 90 psi[3] of chlorine gas. Lower chlorine pressures seriously affect performance and voltage, i.e., a cell discharged at 0.17 amp/cm² gives 1.68 v at 40 psi[4] and 1.83 v at 90 psi[3] or higher.

The over-all performance of this battery has been compiled for a discharge condition where the batteries were discharged at a constant current to a 1.00 v end point at a temperature of 27°C and a controlled chlorine pressure of 90 psi.[3] Fig. 1 gives the watt minutes per cubic centimeter and per gram and Fig. 2 gives the variation in voltage for rates ranging from 0.15 amp/cm³ to 0.61 amp/cm³.

This battery is designed for single continuous discharges of from 1- to 30-minute duration. The construction is of such a nature that the chlorine must be admitted at the time of use. At present, there is no commercial production; however, experimental batteries have been made (8).

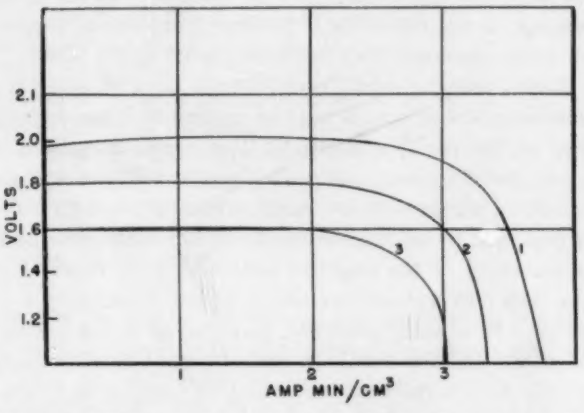

FIG. 2. Discharge characteristics for chlorine-zinc cell. Curve 1—0.15 amp/cm³, electrode current density of 0.0388 amp/cm² (0.25 amp/in.²); curve 2—0.31 amp/cm³, electrode current density of 0.0776 amp/cm² (0.50 amp/in.²); curve 3—0.61 amp/cm³, electrode current density of 0.1552 amp/cm² (1.00 amp/in.²).

[2] 150 psi = 10.52 kg/cm².
[3] 90 psi = 6.32 kg/cm².
[4] 40 psi = 2.81 kg/cm².

REFERENCES

1. D. TOMASSI, "Traité des Piles Electriques," p. 298, Georges Carré, Paris (1889).
2. K. W. ZENGER, German Pat. 26, 819, April 2, 1884.
3. F. FOERSTER, *Z. Elektrochem.*, **29**, 64 (1923).
4. A. SCHMID, *Helv. Chim. Acta*, **7**, 370 (1924).
5. E. BAUR AND J. TOBLER, *Z. Elektrochem.*, **39**, 169 (1933).
6. A. SCHMID AND P. VOGELE, *Helv. Chim. Acta*, **16**, 366 (1933).
7. G. W. HEISE, *Trans. Electrochem. Soc.*, **75**, 155 (1939).
8. G. W. HEISE, E. A. SCHUMACHER, AND N. C. CAHOON, *J. (and Trans.) Electrochem. Soc.*, **94**, 99 (1948).

Thermal Batteries

***Robert B. Goodrich*[1] *and Richard C. Evans*[2]**

Thermal batteries are defined as electrochemical power supplies based upon electrolytes of various inorganic salts which remain solid and nonconducting at all storage temperatures. The electrolyte melts and becomes conducting when the cells are heated to some elevated temperature; electrical energy may then be withdrawn from the system. The features of thermal batteries include good weight and volume factors, shelf stability, temperature range, ruggedness, and versatility in electrical output as the result of a wide choice of electrochemical systems and designs.

[1] National Bureau of Standards, Washington, D. C.
[2] Catalyst Research Corporation, Baltimore, Maryland.

Fused-salt cells, in the general category of fuel cells, have been investigated by Jablochkoff (1), Fabingi and Farkas (2), Jacques (3), Reed (4), Bauer (5), Haber (6), and their associates. Gyuris (7) obtained patents on cells based upon a molten-salt electrolyte with manganese dioxide and molten sodium. Hamer and Schrodt (8) have studied a cell consisting of

Mg, solid or molten electrolyte, MnO_2, C.

The subject has been discussed by Cooper (9), Allmand and Ellingham (10), and Vinal (11). Current efforts are leading to the development of batteries based upon fused-salt elec-

trolytes for applications in the reserve-battery field. Technological success has been achieved to the extent that batteries can now be made to satisfy certain requirements up to 100 watt minutes.

Negative electrodes are normally magnesium or calcium although certain alloys of lithium may be used. This electrode appears to be the controlling factor in the emf of the cell, with calcium giving about one volt more than magnesium. Electrolytes are usually composed of alkali or alkaline earth chlorides, bromides, and nitrates in various combinations. The mode of depolarization, or the chemistry of the positive electrode, is not established. In some instances salts such as potassium chromate may be incorporated in the electrolyte; in others, tungstic oxide, molybdenum trioxide, and similar insoluble oxidizing agents may be applied as a coating to the metal of the positive electrode. This metal may be silver, copper, nickel or iron, and probably others. Processing areas require maintenance of low relative humidities, e.g., 5 to 10 per cent, due to the hygroscopicity of the electrolytes and to the reactivity of the negative electrodes with water. When these cells pick up moisture they are characterized by a cold voltage, i.e., a water potential; this voltage is not sustained under load and the condition leads to rapid deterioration of the cells. An integral heat source may be based upon a variety of exothermic chemical reactions using gaseous, liquid, or solid fuels while the external sources may use these fuels directly or the heat from any available supply. The source must supply sufficient heat to raise the cell temperature above the melting point of the electrolyte which may be from as low as 150°C (302°F) to higher than 600°C (1112°F).

Thermal cells for reserve power supply applications show no unique discharge characteristics. Open-circuit voltages may be as high as 3.0 volts per cell with the working voltage being lowered as a function of the discharge rate. At a current density of 1.6 amp/dm² (0.1 amp/in.²) this drop will approximate 10 per cent, increasing to about 20 per cent at a current density of 7.8 amp/dm² (0.5 amp/in.²). These figures are only indicative of the general performance and vary as a function of design, manner of heating, etc. Over the operating temperature range of a given system, the effect of temperature on the voltage performance is a minor factor.

A summary description of a single cell will indicate the general type of construction and the form of the various components. Many other designs will suggest themselves. This particular cell has the following characteristics and properties:

Open-circuit voltage	2.8
Working voltage	1.8 ± 10%
Load	0.18 ohm
Life	5 min at 400°C
Size (excluding a heat source)	5.10 cm diam x 0.90 cm high
Weight (excluding a heat source)	38 grams

Cell components and assembly:

(1) Sheet calcium negatives with spot-welded nickel leads
(2) Nickel screen positives coated with a fused layer of 80 per cent tungstic oxide with 20 per cent lead chromate.
(3) Glass cloth electrolyte carriers (and/or separators) impregnated with molten salt composed of 55 per cent potassium chloride and 45 per cent lithium chloride.

These parts, on the order of 5.0 cm in diameter by 0.025 to 0.05 cm thick are assembled in parallel using a layer-built design in a nickel can. The battery consists of 5 positive and 6 negative plates, with the depolarizer-coated, inner can surface supplying two additional positive plates. When discharged at the current density of 0.54 amp/cm² (4.6 amp/dm²), the energy amounts to 4.89 watt min/cm³ or 2.37 watt min/g.

REFERENCES

1. M. P. Jablochkoff, *Compt. rend.*, **85**, 1052 (1877).
2. Fabingi and Farkas, *Electrician*, **21**, 169 (1888).
3. W. W. Jacques, *Electrician*, **36**, 768 (1896).
4. C. J. Reed, *J. Franklin Inst.*, **142**, 1 (1896).
5. E. Bauer, W. D. Treadwell, and G. Trumpler, *Z. Elektrochem.*, **27**, 199 (1921); E. Bauer and Tobler, *ibid.*, **39**, 169 (1933)
6. F. Haber and G. W. A. Foster, *Z. anorg. Chem.*, **51**, 245 (1906).
7. J. Gyuris, U. S. Pat., 2,081,926, June 1, 1937; 2,102,701, Dec. 21, 1937.
8. W. J. Hamer and J. P. Schrodt, *J. Am. Chem. Soc.*, **71**, 2347 (1949).
9. W. R. Cooper, "Primary Batteries," p. 415, "Electrician" Printing and Publishing Co., London (1916).
10. A. J. Allmand and H. J. T. Ellingham, "The Principles of Applied Electrochemistry," p. 217, Longmans, Green & Co., New York (1924).
11. G. W. Vinal, "Primary Batteries," p. 324, John Wiley & Sons, Inc., New York (1950).

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Technical Review

The Potential and Coulombic Capacity of Some Galvanic Cell Systems

Allan Walkley[1]

ABSTRACT

The potentials of metal oxide cathodes vary with electrolyte *p*H and with the structure of the oxide. The potentials developed by the lead accumulator and by alkaline cells with cathodes of the oxides of copper, mercury, or silver agree with those calculated from thermal data. Those developed by the Leclanché cell and the alkaline accumulator do not, the reasons being sought in the complex behavior of the ill-defined hydrous oxides of manganese and of nickel. The specific coulombic capacity of oxide electrodes depends upon the molecular weight or molecular volume of the oxide and the number of its reduction states. During discharge these states may be traversed either consecutively or simultaneously with corresponding differences in cell behavior. Theoretical expectations are considerably modified by polarization, so that in practice capacity is usually a function of the current drain.

Introduction

The number of reactions which can be harnessed in a galvanic cell is in theory very large, yet in practice only a few have proved workable as sources of power. In consequence, a dearth of a small number of strategic materials (1) might well cause drastic changes in our economy. The attempt has been made, therefore, to review the different electrochemical systems and to relate the potentials and capacities observed with known properties of the active constituents. Emphasis has been placed on the Leclanché dry cell throughout, partly because it is the most widely used primary cell of today and because it is being studied in these laboratories (2, 3) along with investigations on the structure and properties of the manganese oxides (4, 5) and graphite (6, 7).

The Cell Potential and the Choice of Materials for Electrodes and Electrolytes

Electrodes.—The tables of standard or oxidation potentials, of which Latimer's (8) is the most complete, indicate the wide variety of possible electrode materials. Because of their mechanical properties and strong tendency to ionize, metals are usually preferred as anodes; yet of these there are few without some obviously undesirable property. The alkali metals and others of high negative potential reduce the water of aqueous electrolytes, but cells with such anodes in liquid sulfur dioxide or liquid ammonia electrolytes have been reported (9). Others like iron may become electrochemically passive at high discharge rates. Manganese, although brittle and film-forming, can now be obtained in a high state of purity by electrodeposition and may warrant re-examination.

The tendency to form protective films is most prevalent in the metals of the "a" series of the periodic classification, while those of the "b" series generally form relatively unstable films (14, 15). It is from the latter group, particularly those with low melting points and high hydrogen overvoltages such as zinc, cadmium, mercury, tin, and lead, that the common anode metals have been chosen. Of these, zinc is used most widely in primary cell systems. It has a standard potential of an intermediate value, a very high hydrogen overpotential, and it dissolves readily anodically over a considerable *p*H range, forming either simple metal ions or zincate ions. However, it is less suitable for the negative element of a secondary cell since it is not readily deposited in its original structural form during the charging cycle.[2]

Attempts have been made to use magnesium as a galvanic anode, apparently with considerable success (16, 17, 18, 19). Its high reversible potential of 2.36 v is never achieved, so that, in practice, anode potentials only 0.3 to 0.8 v higher than those for zinc in the same electrolyte are found.

Although both gaseous (20, 17) and liquid depolarizers (16) are still used, most interest attaches to those cathodes which consist of solid oxides. The reactions which these undergo on reduction are often far from simple but they are of the general type shown in Table II.

For the alkaline cells with cathodes of copper, mercury or silver oxides, and anodes of zinc, the observed potentials are within 50 mv of those calculated from thermodynamic data, assuming the reactions to be of the form,

$$Zn + MO \rightleftharpoons ZnO^* + M \qquad (I)$$

or

$$Zn + M_2O \rightleftharpoons ZnO + 2M. \qquad (II)$$

Similarly the correctness of the reaction proposed by Gladstone and Tribe (38) for the lead accumulator was supported by the close agreement found by Vinal and Craig (39) for the calorimetric and electrometric determinations of its heat content change.

For the air-depolarized cell, the alkaline accumulator, and the Leclanché cell, such confirmation is lacking. The emf of the air-depolarized cell is some 250 mv lower than would be expected from reaction 4 of Table II. This might be accounted for if the oxygen is reduced only as far as peroxide, thus:

$$O_2 + H_2O + 2e \rightleftharpoons OH^- + HO_2^-, \qquad (III)$$

a reaction which Berl (40) has shown to be reversible at certain carbon electrodes, and which, although still in dispute for cells containing acid electrolytes (41), is generally accepted as operative in the conventional alkaline cell (20).

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[2] The replating of zinc has proved quite feasible in alkaline cells, provided an excess of dissolved zinc is maintained in the electrolyte, as in the André, Drumm (21, 22), and similar units (23).

* It makes little difference whether the product is the oxide or hydroxide, since the free energy of hydration is here only 1 or 2 kcal; the same applies to the formation of zincate.

The reasons for lack of agreement in the Leclanché system are complex. There is no one emf which can be said to be characteristic; it varies with the nature and proportions of manganese dioxide, carbon, and electrolyte salts. In the fresh cell the *p*H value is often below that necessary for the precipitation of the hydroxide or some other insoluble zinc compound, and hence the potential in this region varies with the ratio of the activities of hydrogen and zinc ions, as would be expected for a reaction of the type:

$$2MnO_2 + Zn + 2H^+ \rightleftharpoons Zn^{2+} + 2MnOOH. \quad (IV)$$

This ratio depends on the initial electrolyte composition (42) and also on *p*H changes resulting from interactions between the electrolyte, the manganese dioxide, and the carbon. High emf (1.7–1.8 v) is commonly found to be associated with a low *p*H value in the bobbin, due to the use of oxides containing appreciable quantities of exchangeable hydrogen ion; but even when the electrolyte *p*H is high enough to cause removal of zinc ions from solution the cell emf can still vary with the nature of the solid reactant and product. Experiment has shown (42–45, 37) that any one sample of MnO_2 in solutions whose *p*H is high enough to prevent the formation of Mn^{3+} gives potentials conforming more or less to the theoretical relation

$$E = E^0 - 0.06\ pH.$$

Oxides differ chiefly in their E^0 values, those for γ-MnO_2 being about 150 mv higher than those for pyrolusites. Measurements conducted in acid solution to avoid the added complication of a solid reaction product have shown (36) that the E^0 values of reaction 7, Table II, depend on both the structural type of oxide and the value of n in the formula MnO_n. Differences of 50–100 mv were found to occur, the γ-oxides again having the highest potentials. The higher voltages observed in cells containing γ-MnO_2 as compared with those containing pyrolusite are due partly to the higher energy content of the γ-oxide and partly to a lower *p*H value in the bobbin. It has been suggested that high potentials are due to oxygen which, it is assumed, exerts its full reversible potential when sorbed on-MnO_2 (46–48). More experimental evidence is required, however, before the role of oxygen can be assessed.

The cell reaction is not known with certainty, both manganite (γ-MnOOH) and hetaerolite ($ZnMn_2O_4$) having been observed in discharge products (49, 45). Thermodynamic data are not available for these two compounds but an approximate value for the potential in neutral electrolytes can be calculated using recent calorimetric data for bixbyite (α-Mn_2O_3) (50, 51) and pyrolusite (β-MnO_2) (52, 53). The free energy change in the reaction

$$Zn + 2MnO_2 \rightleftharpoons ZnO + Mn_2O_3 \quad (V)$$

is given by

$$\Delta G^0 = G^0_{ZnO} + G^0_{Mn_2O_3} - 2G^0_{MnO_2} - G^0_{Zn}$$
$$= -76.5 - 213.1 + 223.1 - 0$$
$$= -66.5 \text{ kcal; or } 1.44 \text{ v.}$$

TABLE I. *Standard potentials and atomic volumes of some metals of interest in cell design*

	Potential v, hydrogen scale at 25°C	Atomic volume cc/g atom
Potassium	−2.92	45.3
Magnesium*	−2.36	14.0
Aluminum	−1.67	10.2
Manganese*	−1.19	7.4
Zinc	−0.76	9.2
Iron	−0.44	7.1
Cadmium	−0.40	13.0
Tin	−0.14	16.3
Lead	−0.13	18.2
Copper	+0.34	7.1

* The values of Mg and Mn have been calculated from recent thermal data (10–12). The remainder have been taken from Latimer's (8) compilation of selected values. For a recently revised list of the standard potentials of the elements see Bockris and Herringshaw (13).

TABLE II. *Half reactions and oxidation-reduction potentials of various galvanic cathodes*

		Half reaction or couple	E^0_H volts hydrogen scale at 25°C	Type of galvanic cell using cathode in question
Alkaline solution	1	$Cu_2O + H_2O + 2e \rightleftharpoons 2Cu + 2OH^-$	−0.36	Lalande (24, 25)
	2	$HgO + H_2O + 2e \rightleftharpoons Hg + 2OH^-$	+0.10	Ruben-Mallory (26, 27) Vidor "Kalium"
	3	$MnO_2 + H_2O + e \rightleftharpoons MnOOH + OH^-$	+0.17*	Leclanché (28)
	4	$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	+0.40	Air cell (20)
	5	$NiO_2 + 2H_2O + 2e \rightleftharpoons Ni(OH)_2 + 2OH^-$	+0.49	Edison (29) Jungner (30) (alkaline accumulator)
	6	$Ag_2O_2 + H_2O + 2e \rightleftharpoons Ag_2O + 2OH^-$	+0.57	Silver oxide cell (23)
			E^0_A	
Acid solution	7	$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23*	Leclanché, with acid electrolyte (31, 32)
	8	$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$	+1.46	Planté (33, 32) (lead accumulator); lead-perchloric acid primary cell (34, 35)
			E^0	
Potential independent of *p*H value	9	$AgCl + e \rightleftharpoons Ag^+ + Cl^-$	+0.22	Silver chloride cell (19)
	10	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1.36	Chlorine cell (17)

* Calculated from thermal data (36, 37). Remaining values from Latimer (8).

No great error is likely to be introduced by the assumption of an anhydrous product as the free energy of hydration of other hydrous oxides has been shown to be small provided they are in a strain-free state. Energy variations due to strain or to those lattice imperfections characteristic of freshly precipitated substances may, of course, occur in the product formed. A rough approximation to the contribution made by the formation of hetaerolite may be obtained by assuming the free energy change in the reaction

$$ZnO + Mn_2O_3 \rightarrow ZnMn_2O_4 \qquad (VI)$$

is the same as that in

$$MnO + Mn_2O_3 \rightarrow Mn_3O_4 \qquad (VII)$$

viz., $\Delta G^0 = -306.2 + 86.8 + 213.1$
$= -6.3$ kcal; or 0.14 v.

The smallness of this figure may be compared with that for the reaction

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4; \qquad \Delta G^0 = -5.4 \text{ kcal (54)} \qquad (VIII)$$

and is only to be expected since such oxides have a very similar arrangement of close packed oxygen atoms, and conversion from one to the other merely involves the disposition of the smaller metal ions. Moreover, hetaerolite and hausmannite (Mn_3O_4) are isostructural with closely agreeing cell dimensions. Most of the dry cells made in these laboratories from pyrolusites in neutral or weakly acid electrolytes have had emf's within the above range of 1.44–1.58 v.

The variation with pH of the potential of the NiO_n electrode, where $1 < n < 2$, which was studied by Haïssinsky and Quesney (55), was found to be similar to that in the MnO_2 electrode, being represented by a series of parallel lines whose distance apart depended on the mode of preparation of the oxide.

These authors do not give the values of n, but from the manner in which the oxides were prepared the one which showed the highest potential would be expected to have the highest n value. It has been realized for many years that the positive oxide of the alkaline accumulator is neither Ni_2O_3 nor NiO_2; some have suggested a solid solution of the two; others an oxide Ni_4O_7. Little seems to be known about the structure of the higher oxides. The monoxide has the rock-salt structure and preparations with n values below 1.005 are unstable. However, oxygen can be taken into this lattice without any further change in magnetic susceptibility or x-ray diffraction pattern (56); thus several experimenters have reported that even the pattern of oxides of composition Ni_2O_3 show only the lines of NiO. Moreover there appear to be no published data for the structure of oxides approximating the formula NiO_2. In these respects nickel differs markedly from the other commonly occurring transition elements and from lead. Fricke and Hüttig (57) review the literature on the corresponding hydrous oxides but come to no definite conclusions as to their structure. It is, of course, possible that a hydrous oxide consisting largely of tetravalent nickel ions exists but is amorphous to x-rays.[3] If so, the lack of stoichiometry of such oxides as $NiO_{1.8}$ may be attributed to the partial substitution of M^{3+} for M^{4+} and of OH^- for O^{2-}, as in some other oxide systems (59, 36). Others have suggested the extra oxygen may be in solution or existing as a peroxide, O_2^{2-}.

The recent production of an iron oxide with a valence of 4 provides another interesting example of higher oxide structure. The standard potential of the couple

$$FeOOH + H_2O + e \rightleftharpoons Fe(OH)_2 + OH^- \qquad (IX)$$

is −0.6 v, so that a cell using a zinc anode and a hydrous ferric oxide cathode would only give a voltage of approximately 1.2 − 0.6 = 0.6 v. However, Selwood and his colleagues (60) have shown that by the gentle ignition of rutile (TiO_2) impregnated with ferric nitrate, a "supported" oxide is formed capable of 2 stages of reduction. Cathodes of such material were prepared and discharged and it would be interesting to know what potential was attained. From the practical point of view the capacity would be low, for the oxide only contained 8.4 per cent of total iron of which 40 per cent was in the +4 state.

The establishment of the over-all cell reaction, important as it is, still tells nothing of the individual electrode mechanisms. Although more properly the province of cell kinetics, the work of Feitknecht and Grossenbacher (61) on the processes in the positive plate of the lead accumulator is relevant here. As a result of electron micrographic examination they suggest the piecemeal replacement of solid $PbSO_4$ by solid PbO_2. It seems clear that some such highly localized topochemical reaction is necessary in producing the structurally reversible electrodes of secondary cells. Similarly in the solid-solid discharge reaction of the Leclanché cathode it would be interesting to know if hetaerolite or manganite are produced as pseudomorphs. The reverse oxidation of manganite by outward diffusion of a hydrogen ion is considered to account for the occurrence in nature of pyrolusite as a pseudomorph after manganite (62).

Electrolytes.—In most cells the electrolyte functions primarily as a conducting medium, but in a few instances it takes part in the over-all cell reaction and so contributes to the cell potential. Thus the reaction of the lead accumulator is written as

$$PbO_2 + Pb + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O \qquad (X)$$

so that the emf will vary with the acid concentration. On the other hand, the reaction for the alkaline accumulator may be expressed in its simplest form as

$$NiO_2 + 2H_2O + Cd \rightleftharpoons Cd(OH)_2 + Ni(OH)_2 \qquad (XI)$$

and it is found in practice that its emf is almost independent of the concentration of the caustic potash electrolyte used, the small changes observed being probably due to variations in the degree of hydration and composition of the hydrous oxides, and in the activity of water. The hydrogen ion concentration of the electrolyte of a number of galvanic cells can be varied without much change in the over-all emf although the individual electrode potentials change considerably. A decrease in the cathode potential with rise in pH in Zn-MnO_2 cells should theoretically be exactly compensated by a rise in anode potential if some $Zn(OH)_2$ is present to keep the activity product $a_{Zn}^{2+} \cdot a_{OH^-}^{2}$ constant. Moreover, the position is much the same if the zincate equilibrium constant is considered. Since at a working electrode the reaction rate is a function of the potential it may be possible by pH adjustment to speed up the slower of the two electrode processes to some extent. However, the choice of pH value, and of electrolyte composition generally, is more likely to be determined by other considerations, such as the effect of electrolyte composition on the solubility or reactivity of the electrode materials on open circuit, or the effect on anode passivation. Thus nickel dioxide will oxidize water at low pH values, and hence stability

[3] The recent work by Glemser and Einerhand (58) confirms the existence of an amorphous oxide of tetravalent nickel.

of the positive electrode in cells of the Edison or Jungner type can only be achieved in alkaline solution. On the other hand the potential of the lead dioxide-plumbous ion couple is only 230 mv greater than that of the water-oxygen couple in acid solution, so the tendency for the electrolyte to be oxidized is small, even without allowing for the retarding effect of oxygen overvoltage. Thus the strong acids, sulfuric or perchloric, can be used in conjunction with lead dioxide. In strong alkali it is appreciably soluble.

The Coulombic Capacity

Ranking equal in importance with the intensive factor, potential, is the extensive factor, capacity.

It is clear from Faraday's law that the number of coulombs (C) of current produced by the anodic solution of 1 cc of a metal is given by

$$C = \frac{z\mathbf{F}\rho}{A}$$

where ρ is the specific gravity of the metal, A its atomic weight, and z the valence change. Values of the atomic volumes, A/ρ of various metals are given in Table I where it will be seen that zinc has a favorable low value. The extreme values of $z\rho/A$ for the metals of Table I are 0.3 for aluminum and 0.02 for potassium.

TABLE III. *Coulombic capacity factors of some metal oxides.* [*The specific gravities are from the compilation by Biltz (63)*]

Oxide and reduction product	Number of Faraday's per mole z	Molecular wt M	Specific gravity ρ	Molecular vol $\frac{M}{\rho}$	$\frac{z\rho}{M}$
Ag_2O_2, Ag	4	248	7.5	33.2	0.12
HgO, Hg	2	217	11.2	19.3	0.10
PbO_2, $PbSO_4$	2	239	9.6	24.8	0.08
MnO_2, MnOOH	1	87	5.1	17.0	0.06

In some primary cells the cathode is necessarily more bulky than the anode, so that the packing of as much cathode material as possible into a given space is an important factor in performance. Neglecting pore space, the specific coulombic capacity of a cathode is directly proportional to the number of Faradays per mole involved in the reduction, and inversely to the molecular volume of the oxide. The relative importance of these factors is seen from Table III.

When an oxide is capable of more than one stage of reduction, it may go to the lowest stage directly or in steps. Thus, omitting all limitations imposed by the possibility of differing reaction speeds, it is clear that an oxide MO will be reduced directly to the metal as shown in reaction (XIV), only if ΔG_1^0 exceeds ΔG_2^0, i.e., if

$$G^0_{M_2O} > G^0_{MO}$$

$$2MO + H_2O + 2e \rightleftharpoons M_2O + 2OH^- \quad : \quad \Delta G_1^0 \quad \text{(XII)}$$

$$M_2O + H_2O + 2e \rightleftharpoons 2M + 2OH^- \quad : \quad \Delta G_2^0 \quad \text{(XIII)}$$

$$2MO + 2H_2O + 4e \rightleftharpoons 2M + 4OH^- \quad : \quad \Delta G_3^0. \quad \text{(XIV)}$$

Free energy values derived from thermal measurements show $G^0_{Hg_2O} > G^0_{HgO}$, but $G^0_{Cu_2O} < G^0_{CuO}$, from which one might expect mercuric oxide to be reduced electrochemically directly to the metal whereas cupric oxide should first form cuprous oxide. The Ruben-Mallory cell using a mercuric oxide cathode has a flat discharge curve with no breaks in it, in accordance with theory; while the Lalande type gives a lower emf after the higher copper oxide has been reduced to the lower (64). However, since such cathodes consist of a mixture of metallic copper and the higher oxide, their potentials are difficult to interpret, for the system is unstable and the reaction

$$CuO + Cu \rightarrow Cu_2O \quad \text{(XV)}$$

proceeds spontaneously at a rate depending on many factors including the reactivity of cupric oxide (24). The anodic oxidation of silver to silver peroxide also occurs in two well-marked stages, although in the corresponding reduction in the silver peroxide primary cell the two stages are less apparent (23, 65). As in the copper oxide cell, the higher oxide is deposited on the metal itself and once again the system is unstable.

The possible stages in the reduction of manganese dioxide can be represented by the idealized equations given below, the free energy changes being calculated from the thermal data referred to previously.

	$\Delta G^0/z$	E^0_B	
$6MnO_2 + 3H_2O + 6e \rightleftharpoons 3Mn_2O_3 + 6OH^-$	-4.2	$+0.18$	(XVI)
$3Mn_2O_3 + H_2O + 2e \rightleftharpoons 2Mn_3O_4 + 2OH^-$	$+4.2$	-0.18	(XVII)
$2Mn_3O_4 + 2H_2O + 4e \rightleftharpoons 6MnO + 4OH^-$	$+9.1$	-0.39	(XVIII)
$6MnO_2 + 6H_2O + 12e \rightleftharpoons 6MnO + 12OH^-$	$+3.2$	$-0.14.$	(XIX)

Provided some kinetic factor, e.g., rate of diffusion or conductivity of the solid, is not limiting, the cathode potential for any given pH value might be expected to remain steady and then to fall after the loss of 25 per cent and 33 per cent of the oxygen. Such abrupt changes are not apparent, however, since the cell voltage begins to fall immediately by polarization and may sink low enough to end the useful life before the first stage of reduction is complete. By prolonged discharge or by reduction of the amount of manganese dioxide in proportion to the other cell constituents the additional stages of reduction can be achieved. Thus the Leclanché dry cell fails to operate many electrical appliances long before its constituents have been consumed, so that the figures given in Table III show it in too favorable a light. The Ruben-Mallory cell with its small degree of polarization utilizes about 90 per cent of its reactants under normal working conditions and has a specific capacity 5 to 10 times that of a Leclanché. It is also stated (29, 33) that in the usual form of the Edison and lead accumulators only about 20 per cent of the active ingredients suffer change during the normal charging and discharging cycle. The perchloric acid cell, on the other hand, differs from all others so far described in that both anode (Pb) and cathode (PbO_2) are soluble. This results in a specific capacity about double that of the normal lead accumulator (19).

The relationship between the capacity of a Leclanché cell and the current density has been derived empirically by Zimmerman (66), while Coleman (67) has made a detailed theoretical study of the same relation. Over a restricted range of current density, I, the equation $C = K I^n$ holds, where n and K are empirical constants, and C is the capacity. A similar relation for the lead accumulator was found by Peukert (68) many years ago. As Beck and Wynne-Jones (69) have shown for the zinc-lead dioxide cell the relation for different preparations of lead dioxide is not the same and probably depends on the surface area of the oxide. On the other hand, the alka-

line accumulator described by Fay and Drumm (21, 22) is claimed to have a capacity almost independent of the current density.

Since electrodes often consist of porous solids produced by electrolysis or by the compression of powders, it may be the apparent rather than the true density which is of significance in influencing specific capacity. The effect of apparent density and of packing is well shown in the Leclanché system, for manganese dioxide and carbon can occur with a wide range of surface area, and hence of apparent density, depending on their mode of preparation or of occurrence in nature. With finely divided oxides such as those prepared by precipitation, the degree of dispersion within the conducting network of carbon may not be adequate for its efficient utilization. This can be improved by increasing the amount of carbon at the expense of the amount of oxide. Moreover, the amount of electrolyte required to press a cathode will increase with the surface area of the two solids, the effect of each being independent and additive (3), so that in any given volume the space occupied by liquid increases and by solid decreases, as the surface area of the latter increases. For both these reasons the apparent advantage of an increase in specific surface of the oxide is offset by a reduction in the amount which can be introduced.

An ideal galvanic system from the point of view of maximum capacity and minimum wastage of materials would demand, in addition to the requirements already discussed, equivalent amounts of anode and cathode material, so that when the current-producing reaction was complete, both electrodes would be entirely consumed. A situation of considerable practical importance arises when one electrode is discharged further, or is polarized more than another, for in this event the potential of the overloaded electrode changes from the value at which the electrode normally operates, to one at which some other reaction can occur. Thus if all the mercuric oxide in the alkaline-mercury cell is reduced before the zinc is consumed, and the cell is still under discharge, the potential of the cathode will approach that of the anode, viz., 1.2 v, which exceeds the reversible potential of the hydrogen electrode at *p*H 14, plus the hydrogen overvoltage. Hence in cells which have been inadvertently left under load although almost exhausted, hydrogen can be evolved within the steel container used and build up to dangerous pressures. Ruben (26) describes how by appropriate design the zinc anode can be entirely consumed just prior to complete reduction of the oxide. It is claimed that such "balanced" cells may be short circuited for months, after having been discharged normally, without gas generation, distortion, or leakage of electrolyte.

REFERENCES

1. E. Just, *J. Chem. Education*, **26**, 331 (1949).
2. H. R. Skewes, *C.S.I.R.O. Divisional Report*, **65**, 1 (1948).
3. H. R. Skewes and A. Walkley, *C.S.I.R.O. Divisional Report*, **66**, 1 (1948).
4. A. D. Wadsley, *Am. Mineral.*, **35**, 485 (1950).
5. A. D. Wadsley, *J. Am. Chem. Soc.*, **72**, 1781 (1950).
6. R. C. Croft, Thesis, University of Tasmania (1948).
7. R. C. Croft and R. Grenfell Thomas, *Nature*, **168**, 32 (1951).
8. W. M. Latimer, "The Oxidation States of the Elements," Prentice Hall Inc., New York (1938).
9. E. Schaschl and H. J. McDonald, *J.* (*and Trans.*) *Electrochem. Soc.*, **94**, 299 (1948).
10. G. E. Coates, *J. Chem. Soc.*, **1945**, 478.
11. C. C. Stephenson, *J. Am. Chem. Soc.*, **68**, 721 (1946).
12. A. Walkley, *J.* (*and Trans.*) *Electrochem. Soc.*, **93**, 316 (1948).
13. J. O'M. Bockris and J. F. Herringshaw, *Disc. Faraday Soc.*, **1**, 328 (1947).
14. U. R. Evans, "Metallic Corrosion, Passivity and Protection," 2nd ed., Edward Arnold & Co., London (1946).
15. G. W. Akimov and G. B. Clark, *Trans. Faraday Soc.*, **43**, 679 (1947).
16. H. A. Barbian and R. E. McNulty, *Trans. Electrochem. Soc.*, **91**, 387 (1947).
17. G. W. Heise, E. A. Schumacher, and N. C. Cahoon, *J.* (*and Trans.*) *Electrochem. Soc.*, **94**, 99 (1948).
18. R. C. Kirk and A. B. Fry, *J.* (*and Trans.*) *Electrochem. Soc.*, **94**, 277 (1948).
19. J. B. Mullen and P. L. Howard, *Trans. Electrochem. Soc.*, **90**, 529 (1946).
20. G. W. Heise, E. A. Schumacher, and C. R. Fisher, *Trans. Electrochem. Soc.*, **92**, 241 (1947); also G. W. Heise and E. A. Schumacher, *Trans. Electrochem. Soc.*, **62**, 383 (1932).
21. A. J. Allmand, *Nature*, **129**, 386 (1932).
22. J. M. Fay and J. J. Drumm, *Trans. World Power Conf., Stockholm*, **6**, 164 (1933).
23. I. A. Denison, *Trans. Electrochem. Soc.*, **90**, 387 (1946).
24. A. J. Allmand, *J. Chem. Soc.*, **99**, 603 (1910).
25. M. L. Martus, *Trans. Electrochem. Soc.*, **68**, 151 (1935).
26. S. Ruben, *Trans. Electrochem. Soc.*, **92**, 219 (1947).
27. M. Friedman and C. E. McCauley, *Trans. Electrochem.* **92**, 81 (1947).
28. G. W. Vinal, *Elec. Eng.*, **67**, 456 (1948).
29. J. T. Crennell and F. M. Lea, "Alkaline Accumulators," Longmans Green & Co., London (1928).
30. A. P. Hauel, *Trans. Electrochem. Soc.*, **76**, 435 (1939).
31. G. Leclanché, *Mondes*, **16**, 532 (1868).
32. C. Drucker and A. Finkelstein, "Galvanische Elemente und Akkumulatoren," Akad. Verlag, Leipsig (1932).
33. G. W. Vinal, "Storage Batteries," 3rd ed., John Wiley & Sons, Inc., New York (1940).
34. J. P. Schrodt, W. J. Otting, J. O. Schoegler, and D. N. Craig, *Trans. Electrochem. Soc.*, **90**, 405 (1946).
35. J. C. White, W. H. Power, R. L. McMurtrie, and R. T. Pierce, *Trans. Electrochem. Soc.*, **91**, 73 (1947).
36. A. D. Wadsley and A. Walkley, *J.* (*and Trans.*) *Electrochem. Soc.*, **95**, 11 (1949).
37. A. Walkley, Unpublished work, Division of Industrial Chemistry, C.S.I.R.O.
38. J. H. Gladstone and A. Tribe, *Nature*, **27**, 583 (1883).
39. G. W. Vinal and D. N. Craig, *J. Research Nat. Bur. Standards*, **14**, 449 (1935).
40. W. G. Berl, *Trans. Electrochem. Soc.*, **83**, 231 (1943).
41. R. S. Weisz and S. S. Jaffe, *J.* (*and Trans.*) *Electrochem. Soc.*, **93**, 128 (1948).
42. N. C. Cahoon, *Trans. Electrochem. Soc.*, **68**, 177 (1935); **92**, 203 (1947).
43. P. D. Lukovtsev, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 469 (1947).
44. J. Maunsell, Unpublished work.
45. H. F. McMurdie, D. N. Craig, and G. W. Vinal, *Trans. Electrochem. Soc.*, **90**, 383 (1946).
46. C. Drucker, *Z. physik. Chem. Bodenstein Festband*, 912 (1931).
47. S. Kaneko, *J. Soc. Chem. Ind. Japan*, **32**, 120 (1929).
48. M. deK. Thompson, *Trans. Electrochem. Soc.*, **68**, 167 (1935).
49. L. G. Copeland and F. S. Griffith, *Trans. Electrochem. Soc.*, **89**, 495 (1946).
50. H. Siemonsen, *Z. Elektrochem.*, **45**, 637 (1939).
51. M. deK. Thompson, "The Total and Free Energies of Formation of Metal Oxides," The Electrochemical Society, Inc., New York (1942).
52. K. K. Kelly and G. E. Moore, *J. Am. Chem. Soc.*, **65**, 782 (1943).
53. H. Shomate, *J. Am. Chem. Soc.*, **65**, 785 (1943).
54. F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.* (*London*), **160**, 261 (1948).

55. M. Haïssinsky and M. Quesney, *Compt. rend.*, **224**, 831 (1947).
56. W. Klemm and K. Hass, *Z. anorg. Chem.*, **219**, 82 (1934).
57. R. Fricke and G. F. Hüttig, "Hydroxyde und Oxyhydrate," Akad. Verlag, Leipsig (1937).
58. O. Glemser and J. Einerhand, *Z. anorg. Chem.*, **261**, 43 (1950).
59. W. Feitknecht and W. Marti, *Helv. Chim. Acta*, **28**, 129 and 149 (1945).
60. P. W. Selwood, M. Ellis, and K. Wethington, *J. Am. Chem. Soc.*, **71**, 2181 (1949).
61. W. Feitknecht and P. Grossenbacher, *Chimia (Switz.)*, **1**, 117 (1947).
62. H. Strunz, *Naturwissenschaften*, **78**, 89 (1943).
63. W. Biltz, "Raumchemie der festen Stoffe," Verlag von Leopold Voss, Leipsig (1934).
64. M. deK. Thompson, "Theoretical and Applied Electrochemistry," Macmillan Co., New York (1939).
65. J. G. Zimmerman, *Trans. Electrochem. Soc.*, **68**, 230 (1935).
66. J. G. Zimmerman, *Trans. Electrochem. Soc.*, **53**, 103 (1928).
67. J. J. Coleman, *Trans. Electrochem. Soc.*, **90**, 545 (1946).
68. W. Peukert, *Electrotech. Z.*, **18**, 287 (1897).
69. W. H. Beck and W. F. K. Wynne-Jones, *Disc. Faraday Soc.*, **1**, 285 (1947).

Additional References

W. F. Cole, A. D. Wadsley, and A. Walkley, *Trans. Electrochem. Soc.*, **92**, 133 (1947).
A. Keller, *Z. Elektrochem.*, **37**, 342 (1931).
W. S. Parker, M. Cohen, and P. Smith, Royal Aircraft Establishment, Farnborough, Chem. Report, No. 436 (1948).
A. P. Rice, *J. (and Trans.) Electrochem. Soc.*, **96**, 114 (1949).
J. C. Southard and C. H. Shomate, *J. Am. Chem. Soc.*, **64**, 1770 (1942).

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Current Affairs

John Wesley Marden Chosen Acheson Medallist

Award to Be Made in Montreal

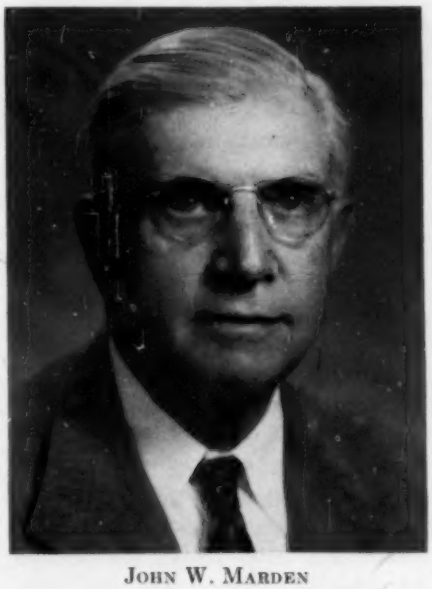
Dr. John W. Marden, recently retired Manager of the Molybdenum Development Division, Westinghouse Electric Corporation, Bloomfield, New Jersey, has been selected as the twelfth recipient of the Edward Goodrich Acheson Medal and Prize. The award, a gold medal and a prize of $1000 is conferred biennially by The Electrochemical Society for the most outstanding contribution to those fields of activity fostered by the Society. The presentation will be made at a banquet in Dr. Marden's honor at the fall meeting of The Electrochemical Society in Montreal.

For most of his long career, Dr. Marden has been concerned with research dealing with the preparation and properties of rare metals and with vacuum tubes, gas-discharge and metal-vapor tubes. He has also been responsible for research in the field of fluorescent powders and their application in fluorescent lamps.

He has long been an active member of The Electrochemical Society and in 1947 was honored at the Louisville meeting by being presented with Honorary Membership. He is also a member of the American Chemical Society, the American Association for the Advancement of Science, the Franklin Institute, Illuminating Engineering Society and the American Institute of the City of New York. Among the Greek-letter societies whose insignia he is entitled to wear are: Sigma Xi, Upsilon Chi, Phi Kappa Phi, Phi Lambda Upsilon, Tau Kappa Epsilon, and Alpha Chi Sigma. Illinois Wesleyan University conferred on him the honorary degree of Doctor of Science in 1946.

Westinghouse awarded Dr. Marden the company's Silver W and Certificate of the Order of Merit in 1944 for distinguished service "for his pioneering work in the production of rare metals and the adaptation of these metals to the advancement of the art of illumination and the science of electrons."

Recently he received from the Department of the Army its highest civilian award, the Certificate of Appreciation, in recognition of his research and development of a new alloy for barrel liners of automatic weapons. He was personally responsible for developing this new alloy which is superior to those currently available.



JOHN W. MARDEN

John Wesley Marden was born May 11, 1887, in Saginaw, Michigan. He attended school there and in Bloomington, Illinois. He obtained his B.S. degree at Illinois Wesleyan in 1908 and continued there as assistant in chemistry. After a year at the University of Illinois, he received a fellowship at New York University where he was awarded his M.S. in 1911 and his Sc.D. in 1912, working under Professor Arthur B. Lamb.

He worked in the Food and Drug Department for the state of South Dakota in 1913–14 and taught chemistry at the University of Missouri from 1914 to 1920. Starting as instructor, he was associate professor when he left to join Westinghouse with which company he has been associated for most of his career. From 1922 to 1942 he was assistant director of research of the Lamp Division, after which he became manager of the Molybdenum Development Division. His stay at Missouri was interrupted during World War I for a year's service as metallurgist with the Bureau of Mines in Golden, Colorado, where Dr. Marden studied zirconium. His interest in rare metals was continued at Westinghouse where he worked on titanium, vanadium, thorium, and uranium. Dr. Marden's skill in the preparation of pure samples of uranium was called upon in 1941 when a request for a kilogram of pure metal came in shrouded in secrecy. Not more than a few grams at a time had been produced before. By January 1942, the order was up to six tons and laboratory methods had to be expanded rapidly and secretly to large-scale production. Eventually 60 tons were prepared for use in the Manhattan project.

New Bakelite Fellowship for Mellon Institute

The establishment of a new Multiple Fellowship to develop uses for resins derived from ethylene and acetylene was announced recently by Dr. E. R. Weidlein, President, Mellon Institute, Pittsburgh. The Fellowship is sponsored by the Bakelite Company, a division of Union Carbide and Carbon Corporation, New York, and will be headed by Richard W. Quarles, Senior Fellow. His associates will be William H. McKnight, Edward T. Severs, Walter K. Vollmer, Arthur C. Frechtling, John T. Ingram and Gordon P. Bigelow.

Fall Meeting in Montreal

This fall members of The Electrochemical Society will meet in Canada for the tenth time. Plans for the 102nd meeting, to be held in Montreal on October 26–30, with headquarters at the Sheraton-Mount Royal Hotel, are now taking definite shape under the guidance of a local committee composed of practically all of the small group of members located in the vicinity of Montreal.

The last meeting held in Canada was in Toronto in the fall of 1946, while almost twenty years have passed since members last met in Montreal, in the spring of 1933. In the interim other Canadian meetings were held in Niagara Falls and in Ottawa.

The city of Montreal, while maintaining its position as an industrial and financial center, has preserved, largely through the influence of its dual French-English culture, a character and charm of its own which distinguishes it among North American cities. Located on an island at the juncture of the Ottawa and St. Lawrence rivers, with the Laurentian Mountains as a backdrop and the unspoiled slopes of Mount Royal rising in the heart of the city, Montreal offers the visitor scenic beauty, many points of historical interest and significance, the best of cuisine, and excellent hotels, shops, and entertainment facilities. These attractions, combined with the promising program of technical meetings, plant and University visits, and social functions now in preparation, are expected to draw a large registration and to result in a most successful meeting.

Nakash, Montreal

A. W. Whitaker, Jr.
General Chairman, Local Committee

Convention Headquarters

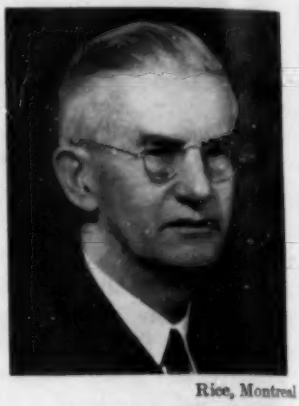
The Sheraton-Mount Royal Hotel, located at the corner of Peel and St. Catherine Streets, in the immediate vicinity of all air and rail terminals and within a short block of the center of Montreal's shopping and theater district, has been selected as Convention headquarters. Registration, social functions, and most, if not all, technical sessions will be held at the headquarters hotel. As usual, reservation of hotel accommodations at an early date is strongly recommended by the local committee and should be sent directly to the Sheraton-Mount Royal Hotel.

Plant Trips

It is anticipated that at least two organized plant or laboratory visits, will be available to interested members during the meeting. The local committee is also completing plans for a visit to the hydroelectric and electrochemical installations of the Saguenay Valley. This trip is described briefly in the July Journal (see p. 165C) and full details are expected to be available for publication in the next issue. Advance registration will probably be required.

Social Functions and Ladies' Program

The Montreal Ladies' Committee is working out details for an interesting and varied program for the entertainment of ladies attending the fall meeting and are adjusting this program to the plans of the Entertainment Committee. The latter tentatively includes a luncheon on Monday and dinners on Tuesday and Wednesday, one of which will be the banquet in honor of the Acheson medallist. Both the Ladies' Committee and the Entertainment Committee will have additional details ready for a later issue of the Journal.



Rice, Montreal

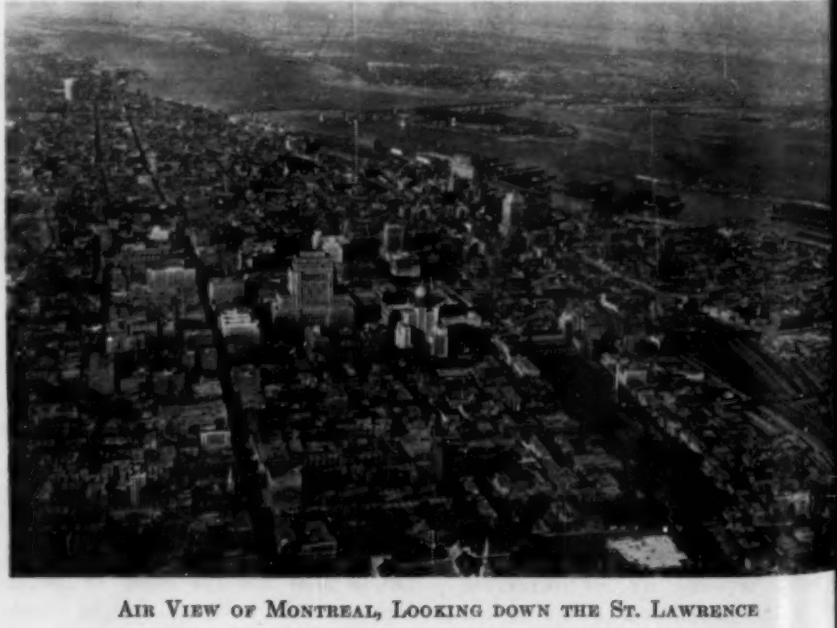
A. F. G. Cadenhead
Assistant General Chairman, Local Committee

Technical Program

The technical program will consist of symposia on Corrosion, Electric Insulation, and Electrodeposition, together with various round tables for these groups. Division chairmen are now arranging their respective sessions.

The Invisible Border

In order to assure re-entry into the United States without inconvenience members entering Canada should carry with them means of identification and preferably some proof of American citizenship. The latter is especially im-



Air View of Montreal, Looking down the St. Lawrence

rtant in the case of those who are merican citizens other than by birth. liens of the United States, resident ere, and coming to Montreal for the eeting should provide themselves in dvance with proof of their right to enter the U.S. Early attention to ese matters is recommended.

ocal Committee Chairmen

Additional information regarding cus-ms, immigration, and financial mat-rs will be published in subsequent sues of the JOURNAL and in the pro-am booklet. Members requiring de-iled information on any points in nnection with the meeting are invited write, in care of the Local Committee ecretary, 1800 Sun Life Building, lontreal, to any of the following local mmittee chairmen: A. W. Whitaker, .—General Chairman; A. F. G. adenhead—Assistant General Chair-an; M. L. Carey—Secretary, Finance ommittee; Mrs. J. U. MacEwan—adies' Committee; J. U. MacEwan—otel Committee; D. F. McNain—egistration Committee; C. Bruce rown—Entertainment Committee; A. Edwards—Publicity Committee; R. Rimmer—Reception Committee.

ifth Empire Congress n Australia in 1953

The Fifth Empire Mining and Metal-rgical Congress will be held in Aus-alia and New Zealand during April nd May, 1953. The object of the ongress is to afford an opportunity r mining engineers, metallurgists, emists, scientists, and others con-rned with the mining and metal-rgical industries to meet and discuss chnical progress and problems, in-uding the development of the mineral sources of the British Commonwealth Nations.

Those interested in complete details the program, travel arrangements, c., should communicate with The ecretary, Fifth Empire Mining and letallurgical Congress, Osborne House, 0 Little Collins Street, Melbourne, ictoria, Australia.

STM Changes 1953 nnual Meeting Date

The American Society for Testing Materials announces that it has changed e date of its Annual Meeting for 1953 om June 22–26 to June 29–July 3. he meeting will be held at Chalfonte-addon Hall, Atlantic City, New ersey.

Eagle Picher—A New Sustaining Member

The Eagle-Picher Company is a producer of lead, zinc, cadmium, germanium, gallium, and their compounds, lead alloys and various metallic products, thermal insulation, home-conditioning materials, paints, pigments, and associated products. About twenty-five plants, scattered over the United States, Canada, and Mexico, are operated by the company or its subsidiaries. The executive offices are in Cincinnati.

Officers heading the company are: T. Spencer Shore, President, and J. M. Bowlby, Chairman of the Board. Vice-presidents in charge of various phases of the company's activities are W. R. Dice, C. A. Geist, M. M. Zoller, and Elmer Isern. R. L. Hallows is Technical Coordinator and Assistant to the President.

The Research Department is located at Joplin, Missouri, with Dr. A. Paul Thompson as director of research and H. R. Harner as assistant director. A staff of over 90 people is engaged in research on primary and secondary batteries, paints and pigments, rare metals, process metallurgy, metal recovery, thermal insulation, and development of new products.

Members of the company's technical staff have long been active in The Electrochemical Society, particularly in the Battery and Electronics Divisions. Dr. J. R. Musgrave is currently chairman of the latter division. The Research Department has one of the best-known storage battery laboratories in the country and much basic data have been published on the lead-acid cell. More recently, Eagle-Picher has pioneered the commercial production of germanium (obtained as a by-product from Tri-State ores) and is a very large producer of this metal, which has had such an impact upon the semiconductor field.

Beckman Forms Division for Custom Instruments

Beckman Instruments, Inc., South Pasadena, California, outstanding for many years in the field of electronic instrumentation, has recently established a new special products division, which will be devoted primarily to the study and development of special instruments brought to it by industrial organizations. J. F. Bishop will direct the new division, which is a completely separate organization within the Beckman Instruments operations. It is located in its own modern plant, with full development and production facilities particularly designed for the manufacturing and testing of custom-built instruments.

Westinghouse Awarded Kaiser Aluminum Order

The Westinghouse Electric Corporation has reported receipt of an order for approximately $9,000,000 worth of electrical equipment for our new pot lines to be installed at the Chalmette aluminum reduction plant of Kaiser Aluminum & Chemical Corporation. Addition of these lines will give the Chalmette plant, located near New Orleans, Louisiana, a total of eight pot lines and will double the plant's capacity.

Each of the four new lines will produce 50 million pounds of aluminum per year, increasing the annual capacity of the plant by 200 million pounds. The operation will be completed by 1953.

$10 Million Expansion for International Graphite

Construction has been started for the new graphitizing facilities which will greatly increase the production of graphite electrodes at the Niagara Falls plant of International Graphite and Electrode Corporation, a subsidiary of Speer Carbon Company, St. Marys, Pa. Covering 25 acres, the expansion is being undertaken to meet the increasing demand of the electric steel and chemical industries.

The new facilities which will cost $10,000,000 include a calciner, 16 graphitizing furnaces, and complete milling, extruding, and baking facilities. It is expected to be in full production by May 1953.

DIVISION NEWS

Theoretical Division

The Nominating Committee of the Theoretical Division of The Electrochemical Society has announced its unanimous agreement on the following slate of officers for 1953:

Chairman—J. P. Fugassi

Vice-Chairman—André J. deBéthune

Secretary-Treasurer—L. B. Rogers

All of the candidates have expressed their willingness to serve. Members of the Nominating Committee are H. H. Uhlig, Chairman; E. L. Eckfeldt, A. Fleischer, and N. Hackerman.

WALTER J. HAMER, *Chairman*

Robert Meeker Wins John W. Marden Prize

Robert Eldon Meeker of Rock Island, Illinois, has been chosen the 1952 winner of the John W. Marden Prize, consisting of a year's subscription to the JOURNAL of The Electrochemical Society. This award is made to the outstanding undergraduate student in chemical engineering at Illinois Wesleyan University during the current year.

Mr. Meeker graduated from Illinois Wesleyan on June 9 with the degree of Bachelor of Science and plans to enter Northwestern University to begin work toward the Ph.D. degree in chemistry.

At college he was elected to Alpha Epsilon Delta, Blue Key, and Phi Kappa Phi, and was reporter for the campus newspaper, the *Argus*. He also won honorable mention in the Seventh Annual Science Talent Search sponsored by the Westinghouse Corporation and conducted by Science Service.

Paul Howard Joins Yardley

Paul L. Howard, well-known electrochemist, has resigned from the Electrochemistry Section of the National Bureau of Standards, Washington, D. C. to accept the position of Technical Director of Yardley Corporation, 105 Chambers Street, New York City. This company is the sole manufacturer of the Yardley Silvercel.

Dr. Howard, a member of the Sub-Panel on Batteries for the Research and Development Board of the Department of Defense, was active in the U. S. Navy's battery development program during World War II, and was consultant on batteries to the Atomic Energy Commission. He was instrumental in organizing the Washington Section of The Electrochemical Society, in which he has been an active worker.

SECTION NEWS

Midland Section

The annual business meeting of the Midland Section was held at White Birch Hills Country Club on June 11. The principal item of business at the meeting was the election of officers for the coming year. The following were elected:

Chairman—Harold H. Roth
Vice-Chairman—W. R. Perry
Secretary-Treasurer—F. N. Alquist

W. R. PERRY, *Secretary-Treasurer*

India Section

The First Technical Meeting of t Section for 1952 was held on May at the Indian Institute of Scien Bangalore, with J. Balachandra in t chair.

V. Aravamuthan (active membe Department of Metallurgy, Ind Institute of Science, read a paper "Economy in the Use of Electricity Many Electroprocesses." The speak stated that the subject is of the utmo importance in starting electrochemic thermal industries in places where t cost of freight on raw materials and f finished products to the principal ma kets are favorable—although the c of electrical energy is not favorable a certain extent.

Economy in the use of electricity electroprocesses can be effected by combination of electro-thermal pro esses in one and the same furnace wi arrangements to collect the produc independently, (2) combination of t chemical with the electrochemi method, (3) substituting the electr chemical by the chemical process, employing electricity on different pri ciples, (5) using electrolytes with low decomposition voltages and (6) e ploying off-peak electricity. Each

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these methods was illustrated in detail.

An interesting discussion then followed and the meeting terminated with a vote of thanks to the speaker proposed by the Secretary.

* * *

The second number (Vol. 1, No. 2, April, 1952) of the *Bulletin of the India Section of The Electrochemical Society* has been issued.

T. L. RAMA CHAR, *Secretary-Treasurer*

PERSONALS

RICHARD F. MARKEL, has left Great Lakes Carbon Corporation at Niagara Falls, N. Y. to join Graphite Specialties Company, also in Niagara Falls.

V. ARAVAMUTHAN has been appointed Senior Scientific Assistant in the Central Electrochemical Research Institute, Karaikudi, India.

P. S. NARAYANA of Mines House, Bangalore, India, has been elected President of the Mysore Geologists Association.

JOHN S. GERRARD, Kuwait Oil Company, Ltd., Kuwait, Persian Gulf, is spending six months in England.

OTIS W. FORTNER, Air Reduction Company, Inc., Murray Hill, N. J., is now at the company's plant at Bound Brook, N. J.

H. JERMAIN CREIGHTON, Professor of Chemistry, Swarthmore College, Swarthmore, Pa., has retired from that college in June and will make his home in Canada at Glen Margaret, Halifax County, Nova Scotia.

JAMES H. BARTLETT, Brookhaven National Laboratory, Upton, Long Island, N. Y., will be located at the Marine Biological Laboratory, Woods Hole, Mass., after August 1.

W. A. KOEHLER, Professor and Head of the Department of Chemical Engineering at West Virginia University, Morgantown, W. Va., became director of the Engineering Experiment Station on July 1. The Experiment Station is the research agency for the College of Engineering and the School of Mines.

WILLIAM D. COOLIDGE, former vice-president and director of research of the General Electric Company, was the first recipient of the K. C. Li Prize and Award, consisting of a gold medal and

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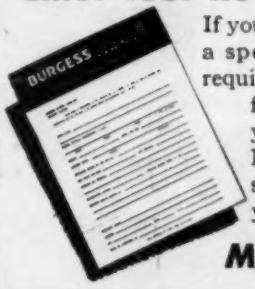

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an honorium of $1000, for his pioneer work on tungsten. The presentation was made at Columbia University on May 20.

P. M. BUHRER has recently been appointed executive vice-president of National Carbon Company, a division of Union Carbide and Carbon Corporation, New York, N. Y.

NEW MEMBERS

In June 1952, the following were elected to membership in The Electrochemical Society.

Active Members

HANNS F. ARLEDTER, Hurlbut Paper Company, South Lee, Mass. (Electric Insulation)

ARTHUR P. BEARD, General Electric Company, mailing add: 828 Hampton Ave., Schenectady, N. Y. (Electronics)

ASAF A. BENDERLY, National Bureau of Standards, mailing add: 1829 Summit Pl., N.W., Washington, D. C. (Electrodeposition)

FRANK C. BENNER, National Research Corporation, mailing add: 25 Colonial Ave., Waltham, Mass. (Electronics and Electrothermic)

WILLIAM K. EARNEST, Pennsylvania Salt Mfg. Company, mailing add: 6400 N.W. Front St., Portland, Ore. (Industrial Electrolytic)

ROBERT L. HADLEY, General Electric Company, mailing add: 1537 Clifton Park Rd., Schenectady, N. Y. (Electrothermic and Rare Metals)

TADAO HAYASHI, Department of Chemistry, Naniwa University, 178, Mozuhigashino-cho, Sakai City, Osaka, Japan (Electro-Organic)

CHARLES C. HOUTZ, Bell Telephone Laboratories, Inc., Murray Hill, N. J. (Industrial Electrolytic)

HITOSHI ISHIKAWA, Nippon Carbon Company, Ltd., No. 1, 1-chome, Shin-Urashimacho, Kanagawaku, Yokohama, Japan (Electrothermic)

LEONARD S. LINCOLN, Pratt & Whitney Aircraft Company, mailing add: 14 Ridgefield St., Manchester, Conn. (Electrodeposition)

TAKASHI MUKAIBOU, University of Tokyo, mailing add: 2-38, Kitazawa, Setagayaku, Tokyo, Japan (Corrosion, Theoretical Electrochemistry)

ATWOOD B. OATMAN, National Carbon Company, 30 E. 42nd St., New York, N. Y. (Electrothermic)

HENRY PAIGE, Naval Air Material Center, mailing add: 6750 Akron St., Philadelphia, Pa. (Corrosion)

PETER W. RANBY, Thorn Electrical Industries, mailing add: 258 Grasmere Ave., Wembley, Middlesex, England

JOHN W. TILEY, Philco Corporation, mailing add: 418 Preston Lane, Hatboro, Pa. (Electronics)

Associate Member

WALLACE L. DRUMHILLER, University of New Mexico, mailing add: 425 W. Santa Fe Ave., Albuquerque, N. M. (Electrodeposition, Electrothermic, and Theoretical Electrochemistry)

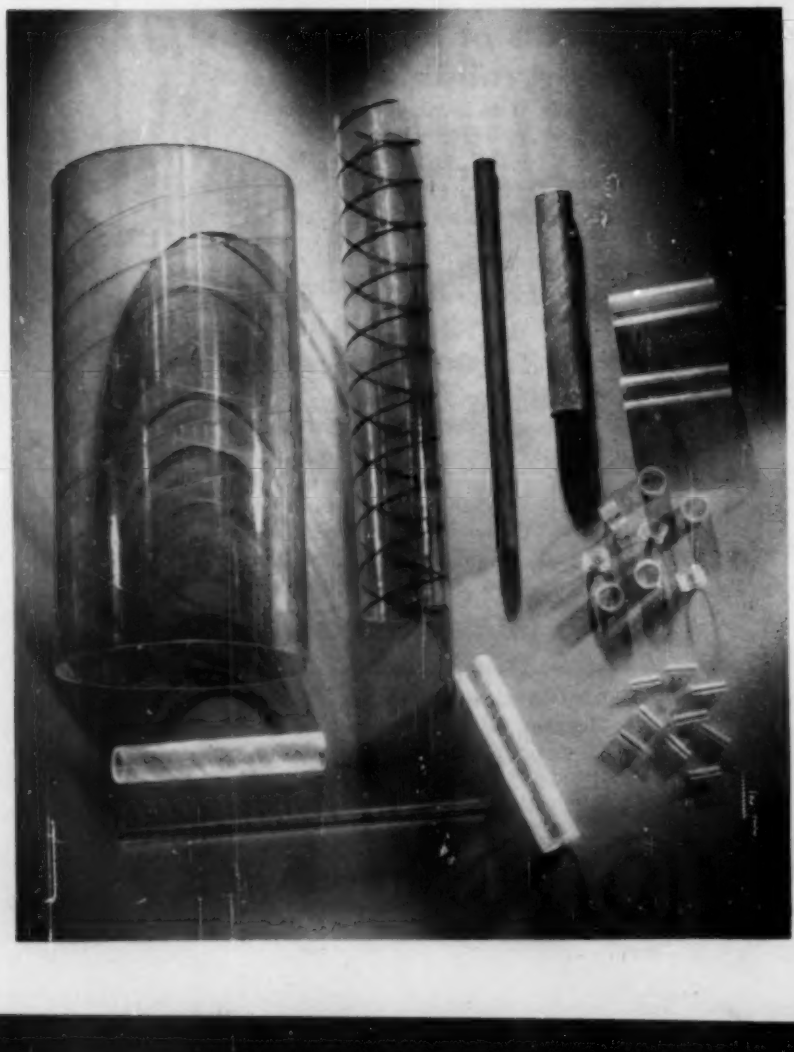
Student Associate Member

DAVID O. FEDER, Columbia University, mailing add: 205 E. 72nd St., New York, N. Y. (Corrosion, Electrodeposition, Electrothermic, and Theoretical Electrochemistry) (Formerly Active Member)

DESMOND M. FEGREDO, Department of Metallurgy, Indian Institute of Science, Bangalore, India (Electrodeposition)

SUNDARESA SOUNDARARAJAN, General Chemistry Department, Indian Institute of Science, Bangalore, India (Electro-Organic)

YEN-NGEN WANG, Missouri School of Mines & Metallurgy, mailing add: 1310 Bishop Ave., Rolla, Mo. (Corrosion and Electrodeposition)



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LETTER TO THE EDITOR

Electrolytic Titanium

Dear Sir:

There is great interest today in the problem of an electrolytic method for producing titanium electroplates or titanium powder. In the course of some work we have done on the electrolysis of titanium compounds in fused salts we have had occasion to check the literature on the subject and find that there is practically nothing of significance in print. We have learned, however, that there are at least a half-dozen different groups working on the problem and that many of them claim verbally to be far advanced in their development. Since none has published anything at all, the danger of duplication and waste in the efforts of each is serious. Although we are at an admittedly early stage in our work, we wish to state our findings in your columns in the hope that others may publish their work and all may benefit—and wasteful "rediscoveries" be eliminated.

We have found that from a bath of the composition shown below, electrolyzed at 850° C in an inert atmosphere at current densities of 30 to 100 amp/dm², titanium powder is deposited on the cathode.

K_2TiF_6	1 part	
NaCl	5 "	(I)
KCl	5 "	

The electrolyte is contained in a graphite crucible which serves as container only and is not in the electric circuit. The powder is deposited as fine fern-like dendrites, together with an impurity insoluble in water and dilute acid. The impurity is observed in the microscope as discrete white particles. Since at 3 amp/dm² no deposit is obtained, but instead the titanium is reduced to the trivalent state, the following trivalent titanium electrolytes were prepared:

$TiCl_3$	2 parts	TiF^3	1.8 parts
NaCl	15 "	NaCl	10 "
KCl	15 "	KCl	10 "
	(II)		(III)

When either of these solutions was electrolyzed at 900° C at 30 to 100 amp/dm², titanium powder was produced at the cathode, but the purity was no greater than previously. Since the impurity is insoluble in water and dilute acid, it must arise from either a contaminated atmosphere or from adsorbed moisture or oxy-compound impurities in the salts, because bath (II), which is composed only of chlorides, contains no insoluble or potentially insoluble ingredients. We believe that elimination of these contaminants will result in essentially pure titanium deposits, as has been found to be true in our work with analogous systems for molybdenum deposition.

FIG. 1. Cross section of titanium deposit, 500×.

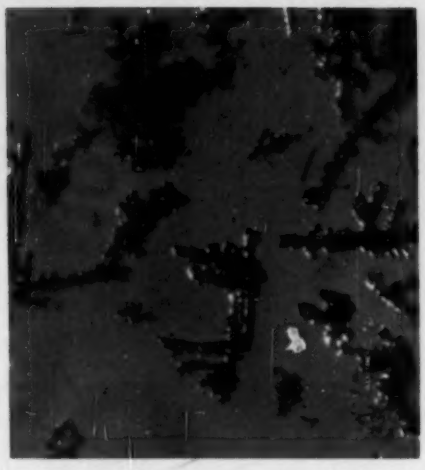

FIG. 2. Titanium powder dendrites, 50×.

We might add that at 100 amp/dm² the cathode current efficiency of bath (II) was over 90 per cent based on the reaction $Ti^{3+} + 3e \rightarrow Ti$. At 30 amp/dm² a tightly adherent layer of titanium metal was found on the tungsten cathode, after the overlying layer of titanium powder was scraped off. The average thickness of this coherent and adherent layer was about 0.0005 inch and seemed to be limited to about the thickness of one or two grains. A photomicrograph of a cross section of this deposit is shown in Fig. 1. Fig. 2 is a photomicrograph of the powder.

We believe that the prospects for the production of pure titanium powder by

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electrolytic means are good. The development of a process for producing a coherent and adherent titanium electrodeposit is important and we hope this note will encourage a greater exchange of information among workers in the field in order to hasten the attainment of these goals.

ABNER BRENNER and
SEYMOUR SENDEROFF
National Bureau of Standards,
Washington, D. C.

BOOK REVIEWS

TABLES OF CHEMICAL KINETICS. HOMOGENEOUS REACTIONS. Circular 510 of the National Bureau of Standards. For sale by Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., xxiv plus 731 pages. 1951. $4.00.

Since the publication of the International Critical Tables in 1926, there has been a tremendous growth and refinement of scientific data. The tables presented in this volume represent a cooperative effort sponsored by the National Bureau of Standards, the Committee on Tables of Constants of the National Research Council, and Princeton University. The tables are delivered in the form of punched loose sheets temporarily assembled under a paper cover. This cover can be removed at the discretion of the subscriber upon receipt of a batch of supplementary sheets which can be inserted in their correct places and the whole set can then be held in a suitable loose-leaf binder.

This volume is essential for all reference libraries.

R. M. BURNS

COTTRELL: SAMARITAN OF SCIENCE by Frank Cameron. Published by Doubleday & Company, Inc., New York, 1952. 403 pages, $4.50.

This very detailed biography of a great scientific humanist and philanthropist makes interesting reading. Since Cottrell kept a meticulously detailed diary from his early student days, through his graduate studies in Europe and down to his death, the biographer was fortunate in finding a vast store of material to draw upon.

To the layman, Cottrell was relatively an unknown; to the chemist, he was perhaps best known by his major contributions to the technology of dust precipitation and of secondary metals recovery. The most valuable contribution, however, that he made to society was his firm and undeviating following-through of an ideal formed early in life. To him profits were not the sole end of his business life. He helped by word or deed hundreds of promising people or their projects.

Cottrell's description of himself as a catalyst for others' activities seems to have been entirely justified. As a matter of fact one of his colleagues is quoted as having said: "Catalyst hell! he's a detonator." A tangible proof of his philanthropic bent was his association with the founding of the Research Corporation and the turning over to it of his early and most valuable patents, among others those important ones dealing with dust precipitation.

Technically he held many important scientific positions including the directorship of the U. S. Bureau of Mines and of the Fixed Nitrogen Research Laboratory. His interests were wide. An individualist in his profession, he was also an individualist in his private life. Science always came first; even the claims of marriage at times had to take second place. Withal he was warm, human, and had a very wide acquaintance and a whole galaxy of friends.

EARLE E. SCHUMACHER

MEETINGS OF OTHER ORGANIZATIONS

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS, general summer meeting, Phoenix, Ariz., August 19–22.

SEVENTH NATIONAL INSTRUMENT CONFERENCE, Cleveland, Ohio, September 8–12.

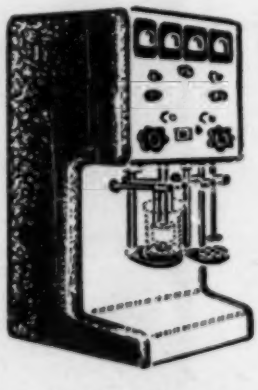
SEVENTH NATIONAL CHEMICAL EXPOSITION, Chicago Coliseum, Chicago, Ill., September 9–13.

AMERICAN CHEMICAL SOCIETY, national meeting, Atlantic City, N. J., September 14–19.

NATIONAL METALS SHOW, Philadelphia Auditorium, Philadelphia, Pa., October 20–24

TENTH ANNUAL PITTSBURGH DIFFRACTION CONFERENCE, Mellon Institute of Industrial Research, Pittsburgh, Pa., November 6–7.

MONTREAL MEETING
of
The Electrochemical Society
October 26-30, 1952
Sessions on Batteries, Corrosion, Electrodeposition, Electric Insulation, Industrial Electrolytics



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RECENT PATENTS

Selected for electrochemists by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

April 22, 1952

Ferrand, L., 2,593,741, Process for the Electrolytic Production of Aluminum

Grolée, J., 2,593,751, Igneous Electrolysis Cell

King, B. H., 2,593,893, Primary Cell

Pavelka, F., 2,593,915, Electro-osmotic Apparatus

Robinson, P., and Reid, C. C., 2,593,922, Insulated Electrical Conductor

Martinez, J. M., 2,594,047, Cathode

Charlesworth, P. A., 2,594,124, Electrolytic Polishing of Metals

April 29, 1952

Baars, E. G., Application 224,440, Method of Impregnating Porous Sintered Nickel Plate

Eastman, E. D., deceased, by Eastman, A. G., executrix, Application 791,465, Electrodeposition of Uranium

Goldowski, N., Application 619,264, Treatment of Aluminum

André, H., 2,594,709, Silver and Zinc Accumulator with Insoluble Negative Electrode and Invariable Electrolyte

André, H. G., 2,594,710, Zinc-Silver Accumulator

André, H. G., 2,594,711, Zinc-Silver Accumulator

André, H. G., 2,594,712, Silver and Zinc Accumulator Having an Insoluble Negative Electrode

André, H. G., 2,594,713, Electric Accumulator

André, H. G., 2,594,714, Method of Forming Electric Accumulators

Stern, C., 2,594,820, Process for Manufacturing Timepiece Dials

Davis, J. N., 2,594,879, Deferred-Action Battery

De Quasie, L. G., and Eisenberg, R. F., 2,594,881, Electrode for Chromium Plating

Knapp, B. B, and Carr, D. S., 2,594,933, Process for Electrodepositing Hard Nickel Plate

Muehlenkamp, G. T., 2,594,972, Electric Furnace

Muehlenkamp, G. T., 2,594,973, Electric Furnace and Lead Electrode

Portail, F., 2,594,988, Primary Battery and Consumer

Wyllie, M. R. J., 2,595,042, Nonpolarizing Electrode for Electric Logging of Boreholes

LITERATURE FROM INDUSTRY

"A-MP Quality Control," a new booklet dealing with quality control of the entire solderless wire termination process has just been published. It provides technical information concerning 3-way control of this process from the raw metal, through manufacture, to the finished installation. Aircraft-Marine Products, Inc. P-47

Adhesion of Hard Nickel to High-Strength Aluminum Alloy. Booklet containing 5 pages, 10 tables, and working drawings describes improved procedure of the well-known zincate process for electroplating on aluminum alloys. Gives satisfactory adhesion and a wear-resistant deposit of hard nickel on a high strength wrought zinc-aluminum alloy. International Nickel Co., Inc. P-48

Vacuum Metallizing. Comprehensive brochure entitled "Vacuum Metallizing Today," describes in detail this newest low-cost coating process and how it can be applied to the surfaces of plastics, metals, glass, paper, textiles, leathers, and many other products. Process is thoroughly covered, including pre-treatment, drawing of vacuum, metallizing, and finishing. F. J. Stokes Machine Co. P-49

Instrument Amplifier. An improved instrument amplifier (Model 102 Phantom Repeater) which greatly increases the accuracy of oscilloscopes and vacuum tube voltmeters is described in a new 4-page bulletin. Has an input impedance of over 200 megohms shunted by 6.0 mmf; gains of 1.0, 10, and 100; frequency response from 5 to over 150,000 cps. Keithley Instruments. P-50

Corrosion-Proof Cements. New bulletin providing technical data and information on the four basic types of corrsion-proof cements has just been released. Includes graphic charts showing the temperature range of each cement and resistance to broad classes of corrosives. Also resistance tables. Atlas Mineral Products Co. P-51

Buffer Tablets. Bulletin describes how these buffer tablets offer a more convenient, economical, and a more exact means of doing an old job in a modern manner. Coleman Instruments, Inc. P 52

Combustion Tube Furnaces. Bulletin announces two new model combustion tube furnaces (Types 70-T and 77-T), using a tap changing transformer which provides 36 steps of temperature control. Transformer mounted in the pyramid type base of the furnace making furnace and controls one complete unit, thus doing away with separate rheostats and costly input control devices. Hevi Duty Electric Co. P-

Fluorescence Analysis. New page, amply illustrated folder titled "X-ray Fluorescence Analysis, Non-Destructive Testing at Shop Level" available gratis. Describes the use of high intensity X-ray tubes and high efficiency Geiger counters for non-destructive identification of elements in 3 to 5 minutes after specimens are prepared. North American Philips Co. Inc. P-

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Editorial

Packages of Power

ELECTRICITY in manageable quantity came with Volta's discovery of the pile and crown of cups as sources of current a century-and-a-half ago. The announcement of his famous apparatus which was destined to be the forerunner of modern batteries was followed immediately by experiments of far-reaching importance in England and elsewhere. This was more than a coincidence. It emphasized the vital role that electrical batteries played in an age of rapidly expanding knowledge of electrical phenomena. Not even the advent of electromagnetically-induced current which had its inception in Faraday's great discovery served to replace batteries or to deny the necessity for them as "packaged power." If they no longer serve as practically the only source of electric power, they fill the ever-present need now for sources of power at times and places where other means are lacking, or because of their reliability they serve as safeguards to insure continuity of service. To the general public the storage battery to start motor cars or the dry cell to light flashlamps are the most familiar types, but more than these the less familiar types are many and vital to our present way of life. Military uses for both primary and secondary batteries developed rapidly in recent years and this has created a demand for widely diverse kinds and sizes.

Batteries are typically electrochemical. The chemical energy of the reacting constituents of the individual cells is supplied to the external circuit as electrical energy. In some batteries the reactions are accomplished so reversibly that the battery may receive the electric current and deliver it again efficiently at a later time. The battery does not, however, store electricity as such. Planté who gave to the world the first practicable storage battery at the tender age of 26 years demonstrated the transformations of one form of energy into another. Using the newly invented Gramme generator which was operated by a hand crank, the mechanical energy of turning the crank was converted by the generator into electrical energy and this in turn was supplied to a battery and stored as chemical energy. When the battery was charged and cranking the generator ceased, the battery was left connected to the generator which then began to operate as a motor. The chemical energy of the battery was delivered as electrical energy to the motor and this turned the crank representing mechanical energy. Thus the cycle was completed.

Electrochemical reactions within the battery take place in accordance with Faraday's fundamental laws and the transformations of one kind of energy into another are in accordance with well recognized laws of thermodynamics.

(*Continued on next page*)

Editorial (*continued*)

The nineteenth century was characterized by many inventions in the realm of batteries and the search for new and better types. Few of those we know today were not the subject of experiment then. Volta's pile set the pattern for the first third of the century. Polarization was ever troublesome until the advent of two-fluid cells typified by Daniell's well-known cell. This was followed by other famous batteries of Grove, Bunsen, and Poggendorf—to mention only a few. In the second half of the century came the era of solid oxide depolarizers and the famous cells of de la Rue, Planté, Leclanché, and Lalande. The close of the century witnessed the invention of the pasted plate storage battery and the entrance of Edison into the battery industry with an improved copper oxide primary cell and an alkaline storage battery which he subsequently modified in 1910.

Batteries in common use during the first part of the twentieth century were mainly familiar storage batteries and dry cells with somewhat less familiar air-depolarized batteries and the modernized Lalande cells. From this relatively standardized variety of batteries, the beginning of World War II brought a sudden demand for new types that greatly stimulated research and invention. Some of the reactions known in former years were utilized and some new types appeared. Among those which now concern us are the silver-peroxide batteries, mercury-oxide batteries, cuprous-chloride batteries, magnesium-types of dry cells, chlorine-depolarized cells, revitalized Zamboni piles, fused-electrolyte cells, and new forms of cadmium batteries. The present tendencies are toward maximum power in limited size and the construction for some purposes of minute sizes. Many of these will hardly appear in the civilian economy, but they are important nevertheless.

The Electrochemical Society is properly the forum for the presentation of papers on battery subjects, but it is only recently that the Battery Division of the Society was formed. It is the youngest of the divisions, but it is showing a most encouraging vigor and growth. This division took over the interests and responsibilities of the former technical committee on primary and storage batteries. This committee had yearly reviewed the technical developments of the preceding twelve months, but had assumed little or no responsibility for periodically presenting symposia on battery subjects. With the presentation of two symposia on batteries at the forthcoming Montreal meeting, covering both primary and secondary batteries, the interest and importance of the subject is evident.

—GEORGE W. VINAL

Fiftieth Anniversary

ANNIVERSARY ISSUE ON STORAGE BATTERIES

Introduction

J. C. White[1]

The second portion of the Battery Division's effort in payg tribute to the 50th Anniversary of the Society is directed ward presenting an up-to-date picture of the characterics of presently known types of storage batteries by recogged authorities in each of the specialized areas. No attempt as been made to include a bibliography on each type but ather to draw on the wide experience of each man in his field summarize the best information that is available in order obtain a brief but authoritative picture of each type of orage battery.

It should be understood of course that while most of the formation to be presented in these articles can be found an individual basis either in books, such as those by G. W. inal, in the scientific literature, or in bulletins supplied by e individual battery manufacturers, there has been little fort in the past to present in one place such a composite icture of the characteristics of the various types of storage atteries. The Society has, however, published 65 papers on orage batteries during the 50 years of its existence.

It is believed that such information will be of real value ot only to those who are encountering storage battery probems for the first time but also to those with battery experice who need a ready reference to the possibilities of other ypes of storage batteries.

It should be realized at the start that storage batteries re notorious for their very low energy output per unit eight and volume, but are at the same time unique in that ey become most important where other sources of energy re impossible. As a result, there are no airplanes driven by orage batteries, and there are no submarines, at least up to 952, which are not driven by storage batteries while under ater. Competition between batteries and other sources of ower is limited to a very few applications.

To balance the great weight of storage batteries as a source power, they have certain advantages, namely: they can eliver a large amount of power instantly; they can be overoaded tremendously; they operate at almost any temperaure; they do not give off poisonous gases; they do not conume air; their stand-by loss is minor; and their energy is eadily converted to light, heat, sound, and can operate radio quipment.

Where a storage battery appears to be the best source of ower, the choice of the type of battery may depend on such rosaic quantities as cost, availability, or weight, and it may nvolve other properties not normally considered, such as helf life, vibration resistance, impact resistance, corrosion f surroundings, and behavior at high rates of discharge or ow temperatures.

The lead-acid battery was the first successful storage batery and it was only after many years of development that the alkaline type of storage battery became available. Since that time, shortly after the turn of the century, there have been two other types of alkaline storage batteries developed, the nickel-zinc or Drumm battery and the silver-zinc battery. In addition, a modified form of the nickel-cadmium battery has been developed in which the pocket type of plates has been replaced by a sintered type of plate. The nickel-zinc battery was developed by Drumm in the Irish Free State about 20 years ago for railroad use but apparently has not been successful and, therefore, will not be described here.

An outline for this up-to-date picture of storage battery characteristics naturally divides itself into two main parts, the lead-acid storage battery and the alkaline types of storage batteries. Since the lead-acid storage battery represents by far the larger volume of storage batteries in use, this part has been further divided into the more important types of applications. The alkaline storage battery portion, on the other hand, has been broken down essentially under the various types of alkaline storage batteries rather than by their application. The last two types in this group have only recently become available to a limited extent but represent, however, the only new types of storage batteries which have been developed for many years and are included primarily on the basis of their potentialities in certain applications.

In each part, an attempt is made to give an accurate but brief description of the battery along with some idea of its present commercial importance and the sizes in which it is available. This is followed in most cases by an over-all picture of the battery's operating characteristics such as watts per pound at various discharge times, density, charge and discharge curves, loss of capacity on stand, and, wherever possible, an idea as to the life of the battery under various types of use such as float, over-charging, and cycle services. No attempt has been made to include complete detailed characteristics under all operating conditions, but rather to give an idea of the over-all characteristics and limitations of each type of battery.

Papers included in this issue are as follows:

"The Lead-Acid Automobile Battery" by E. Willihnganz
"Lead-Acid Motive Power and Carlighting Batteries" by H. C. Riggs
"Lead-Acid Stationary Batteries" by U. B. Thomas
"Plastic Container-Electrolyte Retaining Lead-Acid Storage Batteries" by C. H. Endress and C. C. Rose
"Low Discharge Cells" by C. C. Rose and A. C. Zachlin
"The Edison Nickel-Iron-Alkaline Cell" by F. C. Anderson
"Nickel Cadmium Batteries—Pocket Type" by Sven Bergstrom
"Sintered Plate Nickel-Cadmium Batteries" by G. B. Ellis
"The Zinc-Silver Peroxide-Alkaline Storage Battery" by Samuel Eidensohn.

[1] Naval Research Laboratory, Washington, D. C.

The Lead-Acid Automobile Battery

E. Willihnganz[1]

To most people the term, storage battery, means the lead-acid automobile storage battery. This is a small black unit delivering approximately 100 amp-hr at 6 v. It is a specialized type of battery designed to crank an automobile at a low temperature with a minimum battery weight.

Although the design of the battery is determined by the cranking needs of the automobile, the battery performs many other services. Whenever the engine speed is below a certain minimum value, it is the battery which operates the ignition, lights, horn, radio, and some of the instruments.

The size of automobile batteries is specified by the Society of Automotive Engineers which has standardized external

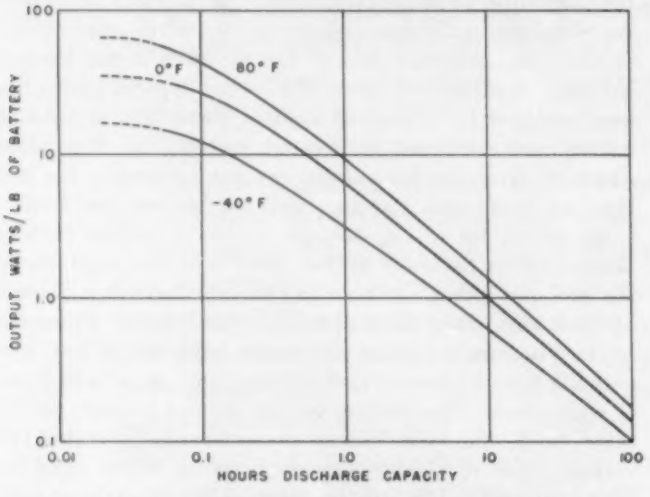


FIG. 1. Power output of automobile type of batteries

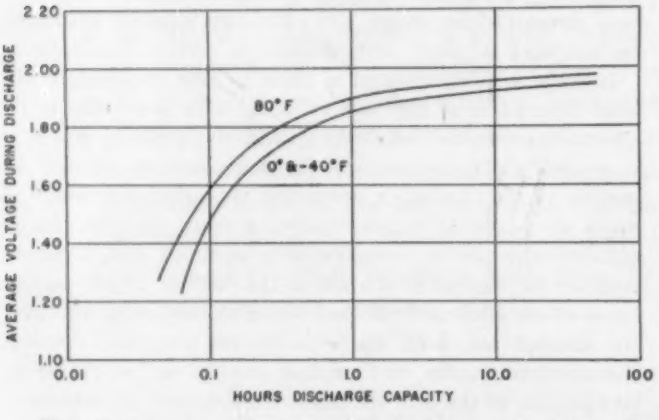


FIG. 2. Average voltage during discharge of automobile batteries.

dimensions and minimum capacity and life ratings of storage batteries which are substantially interchangeable in modern automobiles. Although capacities of 90 to 200 amp-hr are available, at least ¾ of the American battery production is in the 100 to 120 amp-hr sizes. These take care of practically all of the popular automobiles, while the remaining sizes are primarily special-purpose units for truck and bus service.

All of these batteries have essentially the same basic construction. They are of the lead-acid type and have a large number of thin plates in a hard rubber, or equivalent, container with heavy lead connections and lead terminal p adequate to handle a current of several hundred amp They are similar in plate thickness and in separator th ness, but differ principally in the number and size of pla

The electrical size of an automobile battery is usually pressed as its capacity at the 20-hour rate of discharge 80°F. For example, if a battery can be discharged at 5 a for 20 hours before the discharge voltage falls off rapid the battery is rated as a 100 amp-hr battery.

When a battery is being selected for an engineering p pose, it is customary to have in mind a certain load in wa and a period of time during which this load must be livered. For example, suppose that 1200 watts is required 0.1 hour at 0°F. The battery required to deliver this ene can be calculated from the data shown in Fig. 1. Accord to this chart, for a 0.1 minute discharge at 0°F, batteries the automotive type will deliver 26 w/lb of battery. To p duce 1200 w will, therefore, require 1200/26 = 46 lb battery.

The volume of such a battery can be calculated from t weight, since automobile batteries will, in general, wei 138 lb/ft³. Accordingly the volume of the above batte will be 46/138 = 0.333 ft³.

The rated capacity of such a battery, that is, the capaci at the 20-hour rate for a three-cell six volt unit can be es mated on the basis that a 100 amp-hr battery will weigh to 41 lb. The above data has been based on a 38-lb batte weight, so that a 46 lb battery will have a rated capacity 46/30 = 120 amp-hr.

This method of estimating battery size is of general usef ness, but it has some limitations. It can be used to estima the size of a battery required for practically any load a operating temperature. Some variations will occur betwe different brands of batteries. For extremes of battery si the calculated battery weight and volume will be somewh greater or less than calculated. Of course this method of c culation does not tell whether a battery of the desired pow output and case dimensions is actually being manufactur

The excellent capacity at low temperatures and high di charge rates is a gradual development of the last 20 yea and is the result of the presence of materials known as e panders. Where expanders are absent, high rate discharg rapidly coats the sponge lead of the negative plate with a impenetrable layer of lead sulfate which blocks off furth discharge. The expander contains two important ingredient barium sulfate on which lead sulfate can crystallize, and s organic material which prevents lead sulfate from crysta lizing on the sponge lead surface.

The organic ingredient of the expander is, in general, derivative of the lignin fraction of wood and is frequently waste product recovered from a paper mill, although a fe other types of material have been found useful.

Another aspect of battery performance is the voltage du ing discharge. A method of estimating average voltage over mos of the desired range of discharge conditions is shown in Fig. Here again, hours of discharge capacity is used as the hor zontal axis. This is used because it is the quantity specifie in setting up battery requirements, and also because it min mizes the effect of temperature. For example, the averag voltage during a discharge at the 0.1 hour rate is practicall the same whether the discharge is carried out at 0°F or a

[1] Gould-National Batteries, Inc., Depew, New York.

F and is only slightly higher for a discharge of 80°F. course if the discharge rate were expressed in amperes, effect of temperature would be quite different.

Because of the use of a large number of thin plates, the rnal resistance of the cell is quite low and heavy currents be withdrawn without reducing the terminal voltage in cell excessively. In general, this resistance will be approxitely 0.001 ohm per cell of 100 amp-hr capacity at room perature and will be approximately 0.0015 ohm at 0°F. s electrical resistance, however, is not the only reason t the cell voltage is low during discharge. There is also equally important effect due to the slow chemical reacn in the battery. This voltage is called polarization, and, general, acts like an additional electrical resistance. The terms are usually considered together and described as "virtual resistance."

The nature of a polarization within the storage battery has n the subject of much speculation and some experimental k. In general, it is believed that the polarization in the ative plate is due primarily to the presence of lead sulfate olution. The amount of lead sulfate in solution, in turn, ends on the relative rates of the electrochemical reaction which dissolved lead sulfate is produced by discharge and the crystallization rate of this lead sulfate. In the positive te the nature of the polarization has not been studied and s offers one of the main challenges to electrochemistry in aining a very important phase of storage battery operan.

If a charged battery is allowed to stand idle for a period time before being discharged, the capacity declines as the e period increases. This is called self-discharge and may expressed in per cent loss or in terms of specific gravity op. A new battery in good condition with a full charge d an electrolyte specific gravity of 1.280 will drop .030 gr or 20 per cent capacity in a 30-day stand at 80°F. is loss is highly affected by temperature, the rate doung for every 15°F rise in temperature.

Self-discharge usually does not affect the capacity of an tomobile battery in the vehicle since the battery is not le for long periods. However, a battery in transit between e manufacturer and the ultimate user may be idle for veral months. During this idle period, the battery is given charge, at monthly intervals, or is kept fully charged by a all charging unit which continuously supplies enough curnt to offset the self-discharge rate. If an automobile battery used occasionally as a laboratory source of power, but is rmally idle, the self-discharge rate is of considerable imrtance. It is advisable to charge the battery fully after ch period of use and to maintain the charged condition a continuous low rate (trickle charge). The trickle rate ould be sufficient to hold the cell voltage at a value of 20 v. This will require about 0.07 amp/100 amp-hr of pacity.

The major portion of this self-discharge is due to the evolun of hydrogen by the negative plate, and this, in turn, sults primarily from the presence of a small amount of timony. During the process of manufacture of the battery, small amount of corrosion occurs on the positive grid; this leases antimony which is deposited on the sponge lead of e negative plate. This antimony appears to accelerate the lease of hydrogen tremendously.

As a battery ages and more antimony is released by the sitive plate, the self-discharge of the negative plate inreases so that for an older battery more frequent recharge necessary. Where a storage battery is used in an automobile, this self-discharge is normally of very little importance since the automobile generator has sufficient capacity and the automobile is used frequently enough to keep the battery charged.

The life of a storage battery depends principally on the care it receives. A considerable number of automobile batteries have operated satisfactorily for periods of four or more years. Such a life is attained only when the battery is operated at a moderate temperature, is kept fully charged, but is not overcharged.

The charge of a battery in an automobile is controlled by the generator and a voltage regulator which rapidly return current to the battery after the engine is started. The voltage regulator will cut the charge current to a minimum as soon as the voltage of the battery reaches a value slightly greater than the open circuit value of a fully charged battery. If this regulator voltage is set too high, the battery will receive too much charge, will consume considerable water, will operate at a high temperature, and will suffer premature failure due to grid corrosion.

If the voltage regulator is set too low, or if the generator is inadequate for the load being drawn by the electrical equipment of the car, the battery will be undercharged. This is a serious problem for cars equipped with two-way radios, sirens, extra lights, etc., since such cars frequently cruise at low speeds or stand idle for a large fraction of their operating time. Under these conditions the battery gradually is discharged. Such a battery is described as "sulfated" and can often be brought back to operating condition by a long slow charge.

The operating temperature of the battery gives additional troubles.

When a battery becomes overheated, the voltage regulator no longer functions properly. A regulator setting which is perfectly adequate with a battery at 80°F is too high for a battery operating at 140°F and will result in a grossly overcharged battery.

When a battery is operated at a subzero temperature, another trouble occurs. At a low temperature a battery no longer accepts a charge normally. Its voltage rises beyond the cut-off point of the regulator long before the battery is fully charged, and prolonged cold weather operation can result in a seriously undercharged battery.

The charging of automobile batteries received renewed consideration several years ago with the development of the so-called quick chargers. These were transformers and rectifiers capable of putting 50 to 100 amp into a battery. These permitted a battery to be partly recharged while still in the automobile and offer a quick emergency source of power. There was some question, however, as to whether they damage the battery. Further studies have indicated that so long as the charging is done without excessive temperature rise or excessive gassing, an occasional quick charge does not harm the battery. Where temperature rise is excessive or violent gassing occurs, it is obvious that the battery is not in a condition to take a charge normally and quick chargers can do extensive damage.

In automobile service, by far the most important cause of failure after a normal operating period is corrosion of the positive grid. The positive active material, lead peroxide, is in direct electrical contact with metallic lead of the grids and might be expected to produce very rapid self-discharge. Fortunately for the storage battery industry, the first step, occurring when such a positive plate is put on charge, is the formation of a thin layer of lead peroxide which allows the

free passage of electrical current between active material and grid, but almost stops the passage of electrolyte.

The problem of grid corrosion in the positive plate is, therefore, to a large extent one of the properties of this lead peroxide film rather than metallurgical structure of the underlying metal.

In certain types of service, particularly those in which the battery is given repeated deep discharges, failure occurs because of the shedding or loss of positive active material. As the battery is given cycles of charge and discharge, particles of lead peroxide flake off from the positive plate and drop to the bottom of the battery. This loss of active material can be retarded by the use of a barrier of some sort, and for the automobile battery, a thin mat or sheet of glass fibers may be used. Such a glass mat also serves to protect separators under conditions where oxidation of wood separators would otherwise occur.

Recent Developments

During the past few years, considerable effort has been extended to improve the storage battery life. Several new separators have been developed, two new grid alloys h been put on the market, and there has been a concerted m toward the adoption of a lower specific gravity of aci the cells. Reducing the acid gravity from 1.285–1.300 d to 1.260 has reduced the battery capacity slightly, but resulted in a better sustained capacity during the life of battery and a reduced rate of grid corrosion. These chan are too recent to have been noticed in average battery p formance, but it is anticipated that during the next years a considerable increase in battery life will be no

From this can be seen that the automobile storage batt is a special-purpose battery designed to deliver large amou of power at a low temperature from a small package. I also the least expensive storage battery available and c therefore, be used wherever a storage battery is nee either to deliver large amounts of power for a short ti or where space or weight is important. If initial cost is n important and an extremely long life or the absolute ma mum in power output is needed, then some other type battery may be superior.

Lead-Acid Motive Power and Carlighting Batteries

H. C. Riggs[1]

A motive-power battery is one which supplies power to move an electric vehicle. Motive-power batteries were first used in 1890 when there were battery-powered street cars, and by 1895 the first horseless carriage was powered by battery and motor. The first industrial truck appeared in 1907 as developed by the Elwell Parker Electric Company to haul baggage for the Pennsylvania Railroad. From this beginning, industry has now reached the point where no company of any appreciable size can function in materials handling without power driven equipment. Likewise, there has been a steady increase in size of load to where there is now equipment that can lift a freight car. The total worth of the industrial and hand truck batteries in operation today is estimated to be close to $100,000,000.

Motive-power batteries are generally construed to be those types designed especially for the operation of:

Electric rider type of industrial trucks and tractors;
Motorized industrial hand trucks;
Storage battery locomotives and shuttle cars—mine locomotives and shuttle cars, industrial and railway switching locomotives;
Electric power sweepers;
Electric street trucks;
Electric passenger cars; and
Storage battery cars.

For instance, a rider type of industrial truck must have a source of peak power for acceleration during both lifting and running, as well as the ability to withstand daily deep discharging and subsequent charging. During such cycles there is a tendency for the positive active material, the lead peroxide, to become detached from the surface of the plate and fall to the bottom of the jar. In motive-power batteries this loss of active material is retarded by the use of a barrier which holds the active material in contact with the conducting members during the long cycle life with its attendant shocks, vibration, and possible abuse. There are two m methods of retaining positive active material: the slot tubular construction and the more recent use of a glass fi mat next to the active material, and by a perforated sh of inert material in combination with a heavy groo separator.

A second design feature of the motive-power battery is use of a positive plate grid structure sufficiently strong, el

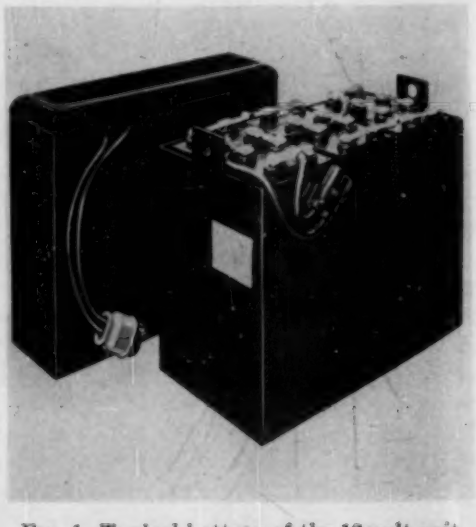


FIG. 1. Typical battery of the 12-volt unit

trically conductive, and corrosion resistant to withstand f action of sulfuric acid and a strong oxidizing environm for five or more years. For strength and corrosion resistan the grid alloy is carefully chosen and, generally, the des is either with heavy core rods for the tubular type plate o heavy lattice grid structure for that type using glass fib

The negative plates for these batteries are, of cour sufficiently thick and durable to match the positives, b do not require the specialized construction.

[1] The Electric Storage Battery Company, Philadelphia, Pennsylvania.

he plates and separators are assembled in the cells with pacity of 100 to 2800 amp-hr.

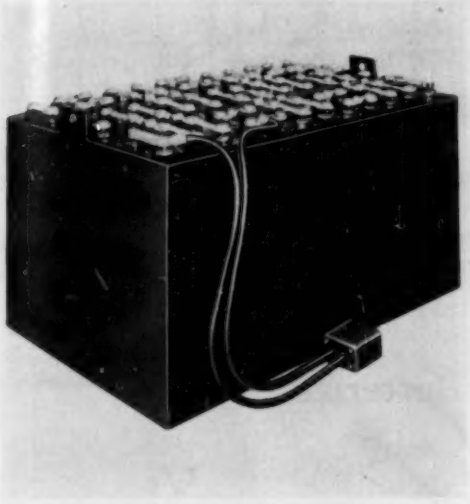


FIG. 2. Typical battery of the 36-volt unit

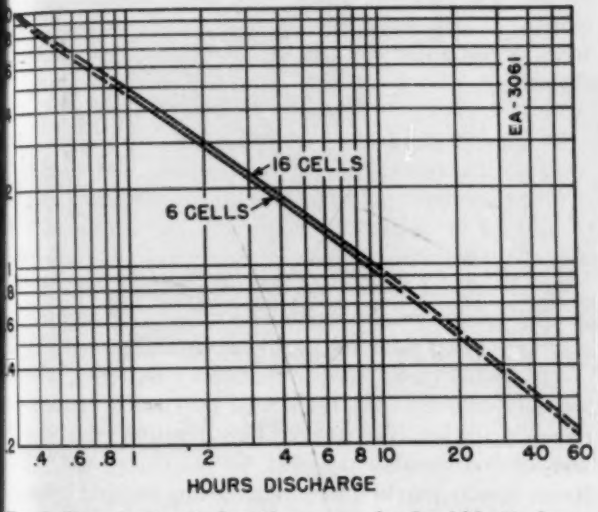


FIG. 3. Power output of motive-power lead-acid batteries

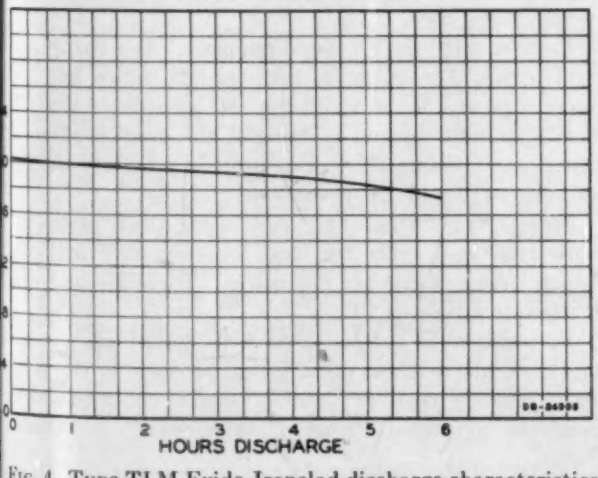


FIG. 4. Type TLM Exide-Ironclad discharge characteristics the 6-hour rate.

Depending upon the type of vehicle it is used with, a bat-ry may consist of from 3 to 240 cells, frequently made up single cells in their individual thin-walled rubber contain-rs and then assembled in either a wood or steel tray such that the entire battery may be handled and connected as a unit. Typical batteries are represented by the 12-volt unit shown in Fig. 1 and the 36-volt unit shown in Fig. 2.

The batteries represented by Fig. 1 and 2 give performances varying with the time of discharge. Fig. 3 shows that

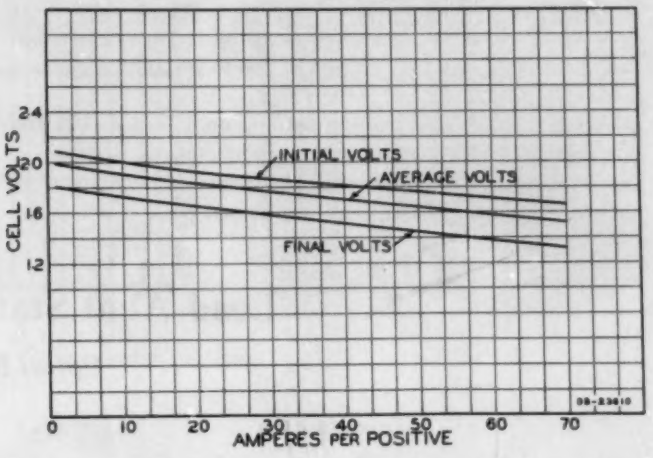


FIG. 5. Type MVM Exide-Ironclad initial, average, and final volts at various discharge rates.

TABLE I. *Motions made by truck in replacing loaded skid with empty at a machine*

1. Stops nearby with empty skid; 2. lowers empty to floor; 3. backs 10 ft without load; 4. stops; 5. goes forward 10 ft without load; 6. stops under loaded skid at machine; 7. lifts loaded skid; 8. backs 10 ft with loaded skid; 9. stops; 10. lowers loaded skid to floor; 11. backs 10 ft without load; 12. goes forward 10 ft without load; 13. stops under empty skid; 14. lifts empty skid; 15. goes forward 10 ft with empty skid; 16. stops; 17. lowers empty at machine; 18. backs 10 ft without load; 19. stops; 20. goes forward 10 ft without load; 21. stops under loaded skid; and 22. lifts loaded skid.

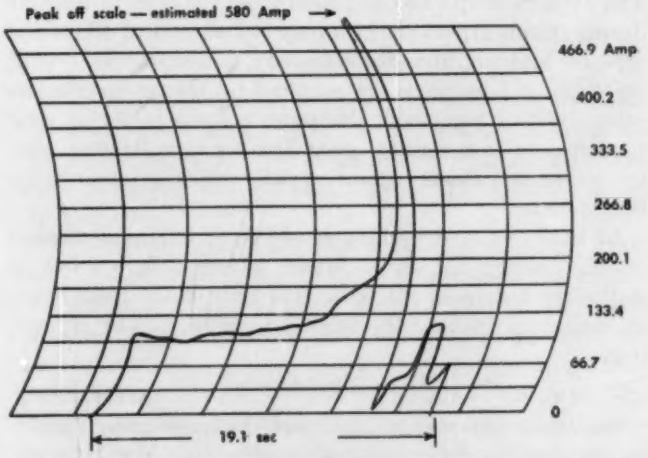


FIG. 6. Recording of a typical run of a 6000-lb industrial truck using a 500-amp-hr battery to raise a 4600-lb load off the floor, tilt the load, and then travel 100 ft.

power output increases with the shortening of the discharge time. The pounds per cubic foot vary from 135 for the 12 volt to 165 for the 36 volt. Just as the watt-hours vary with discharge time, so, too, its component voltage varies with discharge time as in Fig. 4. Voltage also varies with rate of discharge and is shown in Fig. 5.

These discharge voltages and capacity ratings are not the entire story, however. They are measured during a constant current discharge, while, in actual use, the discharge is intermittent. Consider, for instance, the operation of an electric truck which goes to a machine and replaces a loaded skid with an empty at the side of the machine. Table I gives a breakdown of the operations for such a typical trip. Here we have 22 separate operations required to replace a single skid. A working day may consist of 100 to 200 such sequences of operation.

During a single operation of picking up a loaded skid and moving it to a new location, the current demand is shown in Fig. 6. Reading from right to left, there is first, a peak in starting the motor. Then there is a second peak in which the load is lifted. Then a lower peak in which the fork is til back and finally, an extremely high peak in which the tr is started, the entire sequence of operations taking less th 20 sec. Here again it is observed that the battery must sup current in relatively high peaks with some rest periods between, but that the entire day's operations should classed as stop-and-go driving.

For this type of service, with its frequent starts and st and its high peak power demand, the requirements a (*a*) Instant starting; (*b*) high acceleration; and (*c*) suffici stored energy for one shift operation.

In meeting these demands, the motive-power battery made an excellent reputation for low cost reliable long service.

Lead-Acid Stationary Batteries[1]

Upton B. Thomas[2]

Introduction

Stationary batteries, as the name implies, are intended for use in a permanent location. The average driver familiar with his automobile battery may not be aware of the many other uses for storage batteries in our complex electrical civilization. Although by far the largest part of the electrical energy we use is derived from alternating current generators driven by steam or hydroelectric plants, the proper distribution and control of the vast network which distributes this power depends on switches, alarms, circuit breakers, and other battery-operated equipment. The signaling, switching, track control, and communication systems of our railroads are kept at a high level of dependability by the batteries which power them.

Despite the fact that commercial power failures are less frequent and less severe than used to be the case, they still occur. Important equipment such as fire- and burglar-alarm systems, must be provided with emergency battery power. The nation's telephone equipment must continue to function during storms or floods which may cut off central offices and repeater stations from their primary power sources. Public buildings and hospitals are required by law to have emergency lighting equipment. Batteries provide power at locations remote from regular power lines for farm lighting, electric fences, and also for operating radio and other communication systems.

All these and many other uses add up to an annual demand in this country for ten to fifteen million dollars worth of stationary batteries; the individual cells which make them up may vary in capacity from 4 to 7000 amp-hr or even larger.

Design Principles

Stationary batteries do not need the mechanical ruggedness of portable types and their applications do not usually require the high-current output at low temperatures needed for engine starting. Consequently, in their design, it is possible to concentrate on long life, stable characteristics, low self-discharge rates, and high efficiency. Light weight and low first cost can be sacrificed to obtain better over-all performance and lower cost per year of life. These considerations generally lead to the use of relatively thick plates and l gravity acid; glass or plastic jars which would be unsuita for portable batteries can be used. Early stationary batte employed open tanks but these are being replaced by b teries of sealed-jar construction.

Types of Construction

Perhaps 80 per cent of all stationary batteries now be made in this country are of conventional pasted-plate co struction for both positive and negative plates. This type economical of weight and space and less expensive in fi cost than the other types. However, two to three milli dollars worth of stationary batteries using special types positive plates in combination with pasted negatives a currently being produced per year in the United States.

The pasted plates used in stationary batteries, while n basically different from those used in portable batteries, a generally thicker. The design of the positive grids, howeve may be considerably modified for stationary use. The m design usually provides for strengthening the grid by increa ing the cross section of some or all of the cross-member Fig. 1 illustrates several of the types of positive grid cu rently being used.

Certain methods of operation permit the use of speci grid alloys. For example, telephone batteries for flostin service use an alloy in which the lead is hardened with 0.06 0.085 per cent calcium in place of the usual 6–12 per ce antimony. Calcium alloy grids provide a battery with low self-discharge and longer positive-grid life.

Special "Low Discharge" cells using thick pasted plat with pure lead grids are used for stationary applicatio where large currents are not needed. These are described a separate article (p. 243*C*).

In addition to the batteries with pasted positive plat described above, three other types are made in this countr which employ positive plates of special construction. Suc positives are called Planté, "Manchester," or "Ironclad plates.

In the Planté plate the active material is derived fro the metal of the plate itself. For the spun-type plate, a pur lead blank is cast and its surface deeply grooved to increas the exposed area. The grooved plate is treated electrolyti cally to convert its surface to lead dioxide. This type of co struction is illustrated in Fig. 2.

The "Manchester" positive is a variation on the simp

[1] Nickel-alkaline batteries are also used in stationary service but these are described in another article in this issue (pp. 244*C*).

[2] Bell Telephone Laboratories, Murray Hill, New Jersey.

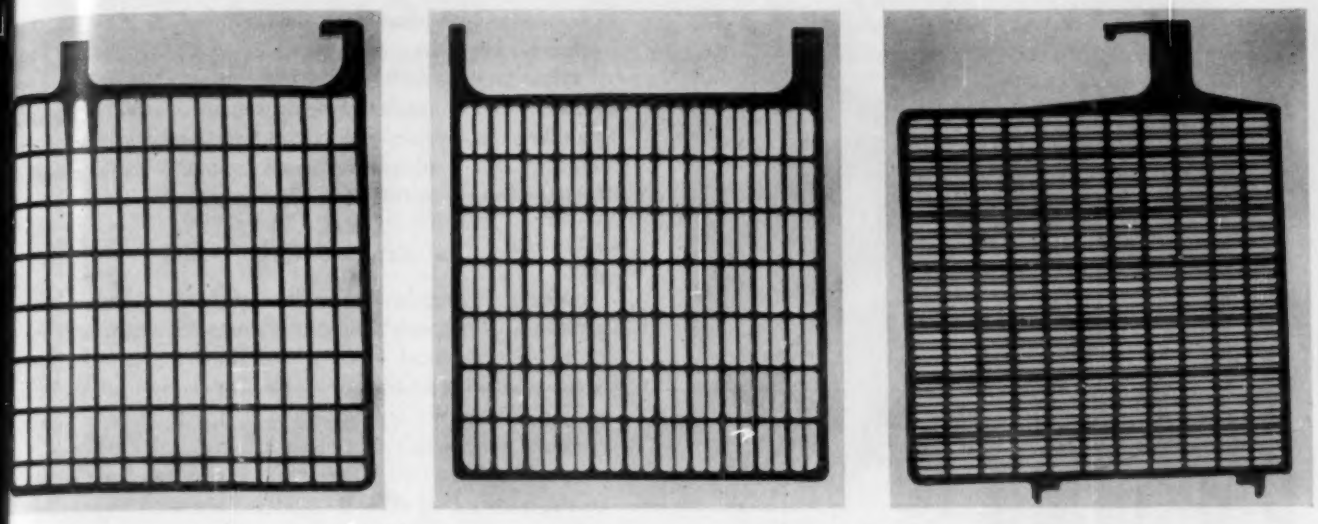


FIG. 1. Positive grids used for stationary batteries

FIG. 2. Spun Planté positive plate, showing grooved surface.

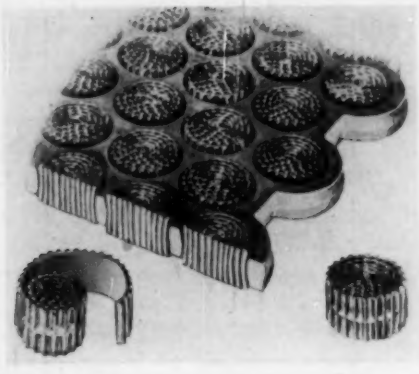


FIG. 3. "Manchester" positive plate with details of construction

Planté. This plate has a lead-antimony alloy grid furnished with a number of circular openings into which are forced "buttons" made from soft lead ribbon corrugated and rolled spirally. The assembled plate is electrolyzed to convert the surface of the pure lead to PbO_2. This process forms a much thinner layer of the dioxide on the alloy grid. A "Manchester" positive plate is shown in Fig. 3.

The long life of Planté positive plates results from the basis of soft lead underlying the active material. As dioxide is lost during the use of the battery, fresh lead is uncovered and converted into additional active material. The excess lead present in a new plate, however, does make such plates heavier than pasted plates of similar capacity.

The "Ironclad" positive, shown in Fig. 4, is of a totally different construction. The basic unit of the plate is a narrow vertical cylinder consisting of a hard rubber tube enclosing the active material which is firmly packed around a central core of lead-antimony alloy. Access to the electrolyte is provided by a large number of fine horizontal slots cut in the hard rubber tubes. The tubes are held together and electrical conductivity is provided by a grid which includes the alloy cores and horizontal members which tie them together. Although the "Ironclad" plate is primarily designed for heavy-duty portable batteries, it is used to some extent for stationary cells.

Separators

The separators used in stationary batteries may be of wood or microporous hard rubber. A new plastic material with properties similar to those of microporous rubber has recently been developed and will undoubtedly find wide use in long-life batteries.

Grooved separators are used with "Manchester," Planté, and pasted positives, sometimes in conjunction with retainers for holding the positive active material in place. The retainer consists of a perforated or slotted sheet of hard rubber, polystyrene, or other plastic. A mat of glass fiber is sometimes used between the retainer and the surface of the plate. "Ironclad" batteries use ungrooved separators, since the plate construction provides acid space next to the positive plate.

Electrolyte

Almost all stationary batteries use low-gravity electrolyte of 1.200–1.225 sp gr. This requires a larger volume than high-gravity acid, but reduces the rate of self-discharge.

Jars

Jars for stationary batteries may be made of hard rubber, glass, or plastic. Cells larger than 180-amp-hr capacity are usually in individual jars, while the smaller sizes may be made in 2- or 3-cell units.

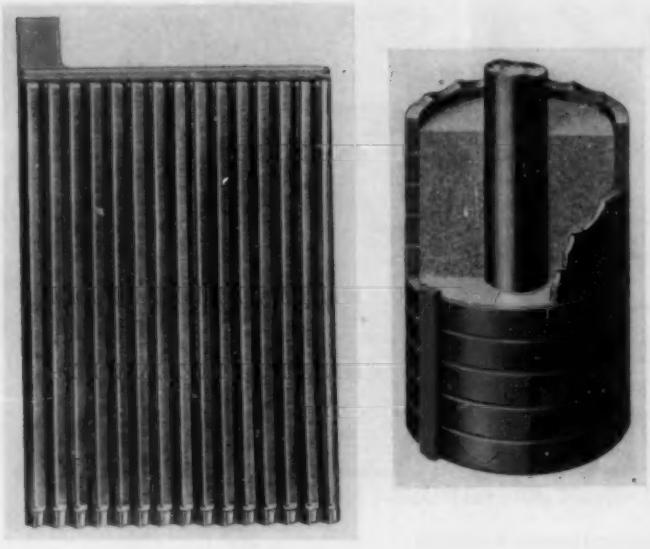


FIG. 4. "Ironclad" positive plate and an enlarged cutaway view showing construction of a tube.

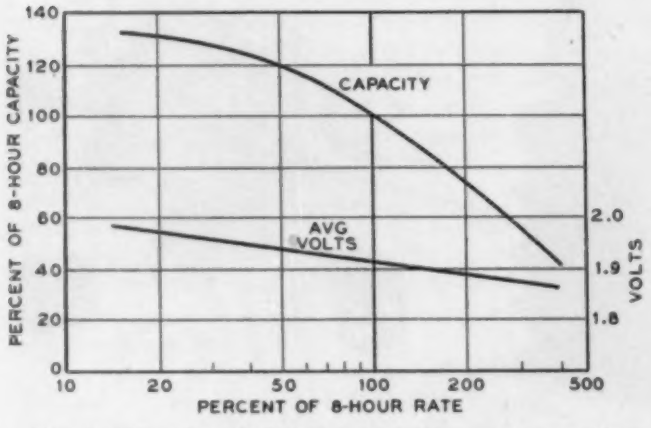


FIG. 5. The effect of discharge current on average voltage and amp-hr output at 77°F to 1.75 volts per cell.

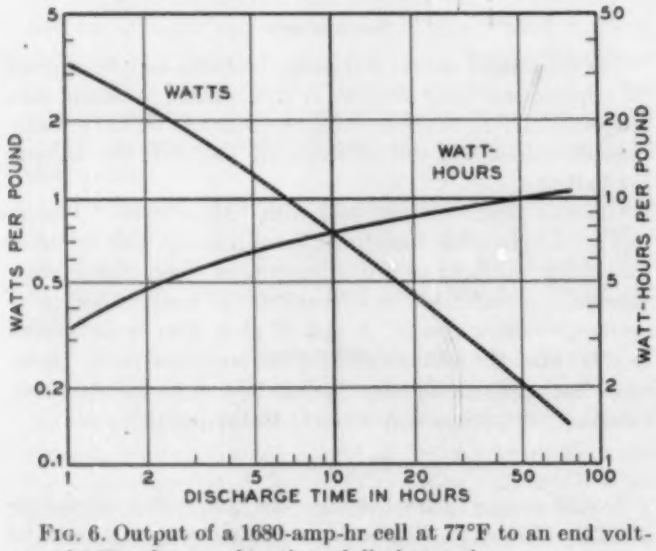


FIG. 6. Output of a 1680-amp-hr cell at 77°F to an end voltage of 1.75 volts as a function of discharge time.

Hard-rubber jars are rugged and easily made in large sizes but have the disadvantage of being opaque. This makes it impossible to inspect the condition of the cell or to observe readily the electrolyte level. The latter difficulty can be circumvented by the use of a plastic or hollow glass float whi extends above the cover.

Glass jars are widely used with either glass or hard-rubb covers but are gradually being replaced, particularly in t smaller sizes, by jars molded from heat-resistant polystyren This plastic is now being used to make jars for batteri ranging from 4 to 660 amp-hr in capacity.

Explosion-proof Vents

Cells of 50 amp-hr and larger used for telephone service a provided with special venting systems to eliminate the poss bility of accidental explosion of the hydrogen and oxyge given off during charge. If a spark or flame from an extern source reaches an accumulation of these gases in the spa between the surface of the electrolyte and the cover of t cell, an explosion may occur which can break either the j or the cover. Two different systems are used to prevent thi One uses an inverted funnel to collect the gases below t surface of the electrolyte and vent them so that the onl place an explosive mixture can exist is in the neck of t funnel. An explosion of this small volume is harmless. Th other method uses a principle similar to that of the Dave Safety Lamp. Gases leave the cell through a porous ceram vent, which prevents the entrance of any spark or flame t the space inside. Both types of cells use filling funnels extend ing below the surface of the acid so that water may be adde or hydrometer readings taken without removing the vent

Battery Characteristics

The capacity of stationary batteries is usually specified by giving the number of amp-hr which can be delivered during an 8-hour discharge to an end voltage of 1.75 volts per cel at an initial electrolyte temperature of 77°F. This is called the rated capacity and the performance under other condi tions may conveniently be referred to this standard condi tion.

For certain special types of application, however, batteries are chosen on the basis of ratings other than the 8-hour one. For example, batteries for switch gear or circuit-breaker operation are selected on the basis of the one-minute rate to 1.75 volts per cell and the selection of emergency lighting batteries is usually based on the three-hour rate.

The performance of a battery is a function of the tempera ture and the current. In comparing cells of different sizes it is often useful to specify not the current but the discharge time to a given end voltage. Stationary batteries are rarely used at discharge rates greater than the 1-hour rate, i.e., the current which would discharge the battery in 1 hour. Occasionally, however, larger currents will be drawn for very brief periods, as for example in operating switches or circuit breakers. The larger the steady current drawn, the smaller the number of ampere-hours available to a given end voltage and the lower the average voltage as illustrated in Fig. 5. The available capacity is also a function of discharge tem perature. For example, a cell giving 100 amp-hr at the 8-hour rate at 77°F will give 86 amp-hr at 50°F and 109 amp-hr at 110°F.

Fig. 6 shows how the output in watts per pound and watt-hours per pound varies with the required discharge time. The curves are based on the performance of a telephone battery of 1680-amp-hr rated capacity having pasted plates and a hard-rubber jar. Other sizes and types have similar curves and these can be calculated approximately from Fig. 6 and the data in Table I.

TABLE I. *Output per unit volume and weight of various types and sizes of stationary batteries*

All cells with pasted negative plates, 1.200–1.225 sp gr electrolyte, discharged to 1.75 volts at 77°F at the 8-hour rate.

Positive plate	Jar	8-hr capacity, amp-hr	Over-all density (1), lb/ft³	Watts/lb at 8-hr rate	Watts/ft³ at 8-hr rate
Pasted	Hard Rubber (2)	4070–6900	123–126	0.86–0.87	106–110
"	" " (2)	840–1680	133–137	0.89–0.97	118–133
"	" " (2)	240–660	118–123	0.79–0.88	93–108
"	Glass	608–1064	151–154	0.80–0.89	121–137
"	" (3)	100	130	0.87	113
"	Plastic (3)	100	118	1.23	145
"Manchester"	Glass	560–960	170–174	0.65–0.71	111–123
Planté	"	480–800	127–131	0.54–0.61	68–80
"Ironclad"	Hard Rubber	750–1000	118–119	0.97–1.00	115–116

NOTES: (1) Volume is calculated as the product of the over-all height, length, and width.
(2) With explosion-proof vent.
(3) 3-cell unit.

TABLE II

Type of cell	Life on float	Life in cycle service
asted plate, lead-antimony grids	14 yr	6–8 yr
asted plate, lead-calcium grids	25 yr (est.)	not determined
Manchester" positives	25 yr	10–14 yr
lanté positives	25 yr	10–14 yr
Ironclad" positives	14 yr	6–8 yr

Self-Discharge

All storage batteries lose some of their capacity while standing idle because of a slow reaction between the sponge lead of the negative plate and the electrolyte. The rate depends on temperature, the age of the cell, and on the materials used in the cell. Standard types of stationary batteries with pasted plates and lead-antimony alloy grids lose approximately 30 per cent of their capacity per month at 77°F. This rate changes by a factor of about two for each 15°F change in temperature. Thus at 92°F the rate is 60 per cent per month and at 62°F only 15 per cent per month. Cells with pure lead plates or lead-calcium alloy grids have self-discharge rates only about ⅕ as great as that of cells with lead-antimony grids.

Cell Life

The service life of stationary cells depends on the service conditions and on the construction of the cells. The longest life is obtained when the cells are "floated," that is they are continuously charged at a rate just slightly greater than that required to overcome self-discharge. Such cells are only infrequently discharged. Cycle service in which the cells are regularly charged and discharged gives shorter life. In any kind of service the life will depend on the temperature and the quality of maintenance. Table II gives some estimated figures for life under ordinary conditions.

Plastic Container-Electrolyte Retaining Lead-Acid Storage Batteries

C. H. Endress[1] *and C. C. Rose*[1]

Lead-acid storage batteries have certain inherent advantages as a portable or stand-by power source, in respect to high voltage, high rate, and low temperature capacity, rechargeability, etc., which make them desirable for many applications other than automobile starting and lighting and similar heavy-duty service.

Their application to these various devices and services has been hindered somewhat by the old hackneyed design of heavy rubber or asphalt composition containers, wood or rubber separators, acid leakage or spillage, and other problems of proper maintenance of an element which cannot be seen, and the state of charge of which is not evident.

All of these objectionable features have been eliminated in the plastic container-electrolyte retaining (ER) batteries.

In general, either polystyrene or Bakelite C-11 plastic is used for injection molding of covers and containers. These materials are light in weight, comparatively strong in thin sections, can be molded easily and rapidly in rather complicated designs within close tolerances, and are completely acid-resisting for this purpose. Design has varied widely, many being for specific applications, but in general it will include an acid well in the cover as part of the nonspill feature and gravity-indicator ball cage either in the cover or the container as the space arrangement may require. Because the plastic container is completely transparent, electrolyte level is clearly indicated at all times and state of charge likewise may be determined by gravity balls chosen to float at full or half charge and to sink at complete discharge. Single or multiple cell units may be molded in an almost infinite range of sizes and still further combinations may be built up for specific applications by the simple expedient of joining individual cells or units with polystyrene cement. Covers are easily and permanently bonded to containers after assembly in the same manner with polystyrene cement, assuring complete freedom from acid leakage.

The electrolyte in these cells is immobilized by the use of Fibrite insulators which absorb at least 90 per cent of the free liquid. Fibrite is a firm but soft sheet of treated redwood bark fibers made by standard paper-making process to required thickness and density, with low electrolytic resistance and good acid stability. It is made in several different thicknesses depending upon the design and purpose of the cell in

[1] Willard Storage Battery Company, Cleveland, Ohio.

question. In those cells used at normal rates and temperatures and with plates of standard thickness, the insulation will last the life of the plates, up to 300 cycles. Fibrite is not suitable for automotive batteries.

One of the first and probably the smallest of these batteries is the Radiosonde unit. The "B" unit of this battery is 18 cell, i.e., 36 v in a container $3\frac{7}{16}$ in. x $1\frac{7}{16}$ in. x $2\frac{29}{32}$ in. and delivers .027 amp for 220 min to 31.5 v at 80°F or for 75 min at −40°F.

There are 40 or more of these special application miscellaneous types and designs in sizes up to 40 amp-hr/cell (Fig. 1). These vary widely in the matter of plates per cell, thickness, and size of grids used, (.040 in.–.140 in.), and Fibrite thickness, depending upon the type of service required. Some of these are intended for maximum capacity

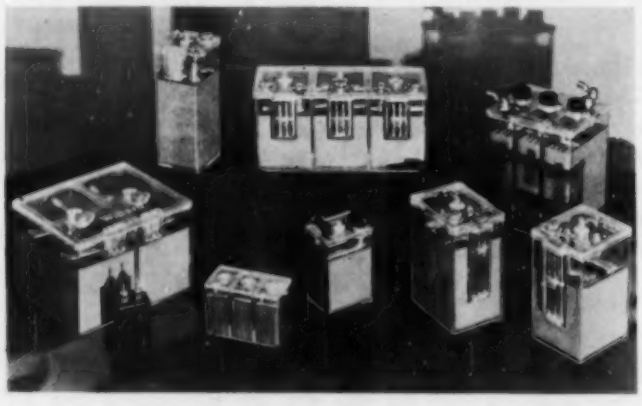


FIG. 1. Typical storage batteries of the electrolyte retaining type.

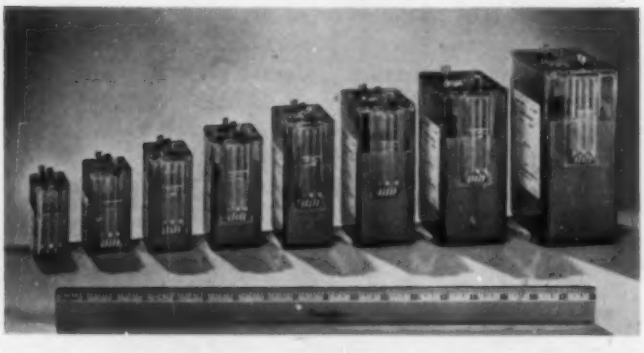


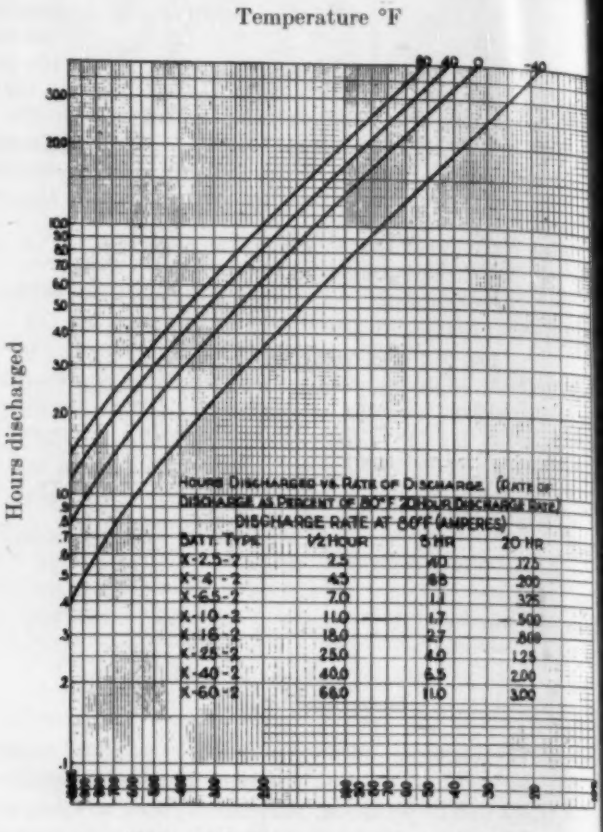
FIG. 2. X-line plastic container ER batteries standardized for Signal Corps use.

one-shot applications and others for more extended life in cycling service.

In addition to this, there is a more standardized line of these cells designed specifically for The Squier Laboratory of the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey (Fig. 2). Capacity varies from 2.5 to 60 amp-hr/cell in eight container sizes designed to dimensions approximately 2 x 3 x 5 ratio. Because of this standardized design the capacity curves of the different sizes are very similar at the various rates and temperatures. Based on per cent of 20-hour capacity at 80°F these curves are accurate within 5 per cent (Fig. 3).

In most respects these ER batteries behave much as other lead-acid batteries. Some slight increase in active material to grid ratio may be obtained in some designs where high capacity is more important than long life. Acid-to-active material ratio is normal and full-charge gravity generally is normal 1.285. Their chief feature, of course, is the saving volume and weight per ampere-hour by virtue of the plas container and cover (Fig. 4).

They may be discharged at high rates without harm, b must be recharged at low rates because of restricted a



Rate of discharge as per cent of 80°F 20 hr discharge rate

FIG. 3. Current output of electrolyte retaining batteries

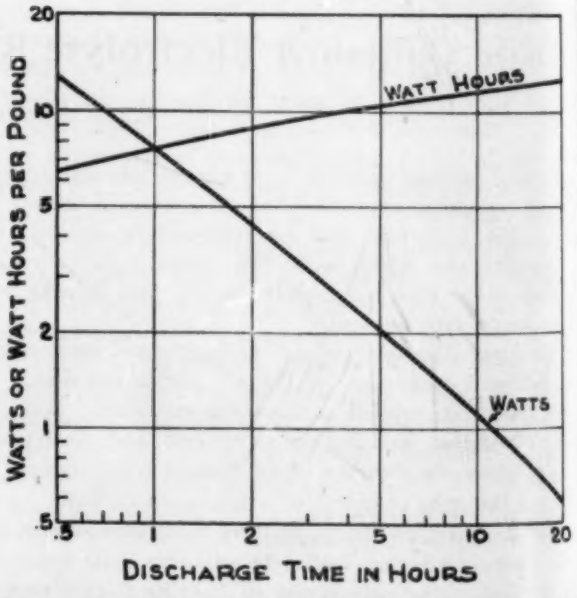


FIG. 4. Typical power output of plastic case ER batteries

circulation. It is important to maintain electrolyte level with water and as always not allow them to stand discharged. They self-discharge at about the normal rate of 1 per cent per day except when special grid alloys are used; then this rate may be decreased about one-third.

Such cells are being used in portable radios, hand lanterns, photographic flash units, telemetering devices, guided missiles, and numerous other military applications. In fact they may be used in any portable power application in place of dry cells, where good high-rate capacity, high voltage, and rechargeability offer definite economic advantages.

Low Discharge Cells

C. C. Rose[1] *and A. C. Zachlin*[1]

Low Discharge, i.e., charge-retaining lead-acid storage batteries, were introduced in 1933 (1) and, judging from a steadily increasing demand, have found many fields of useful application.

These cells are characterized, as the name implies, by a low rate of self-discharge, achieved mainly by the use of pure

TABLE I. *General data on "LD" cells*

Cell type	DA-2-1	DD-5-1	DH-5-1
Height	$6\frac{11}{16}$ in.	$9\frac{1}{2}$ in.	14 in.
Length and width	$2\frac{1}{2}$ in. x $2\frac{1}{2}$ in.	$5\frac{1}{2}$ in. x $7\frac{1}{16}$ in.	$7\frac{5}{16}$ in. x $8\frac{5}{16}$ in.
Volume, in.^{3}	37	282	555
Initial open-circuit volts	2.14	2.14	2.14
Weight, lb	$3\frac{1}{2}$	26	58
Test rate—amp	0.100	0.500	1.00
Approximate average voltage at test rate of discharge to:			
1.95 v cutoff	2.05	2.05	2.05
1.8 v cutoff	1.97	1.97	1.97
Amp-hr capacity to:			
1.9 v cutoff	26	200	540
1.8 v cutoff	30	220	600
Watt-hour to 1.8 v	59	433	1180
Watt-hour/lb	16.85	16.65	20.3
Continuous discharge rates, amp	0.015	0.075	0.250
Charging rate, amp	1.0	5.0	10
Approximate charging time, hr	48	55	75
Full charge specific gravity	1.300	1.300	1.300

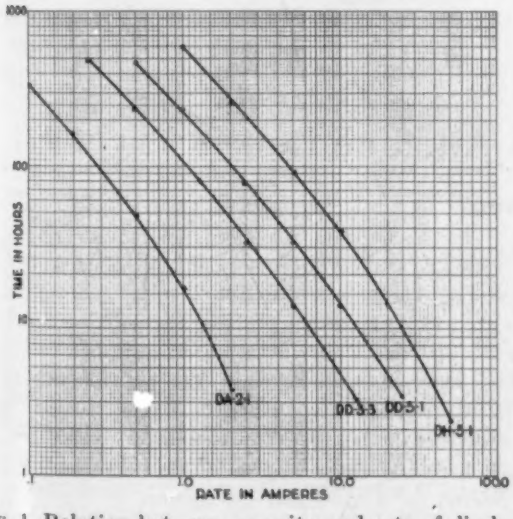


FIG. 1. Relation between capacity and rate of discharge of LD cells at 80°F to cutoff voltage of 1.80 v/cell.

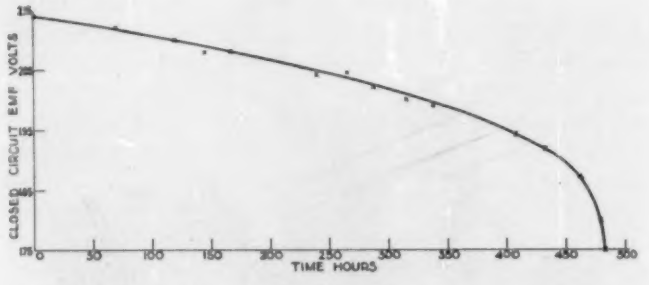


FIG. 2. Discharge voltage of a DD-5-1 cell at .500 amp at 80°F.

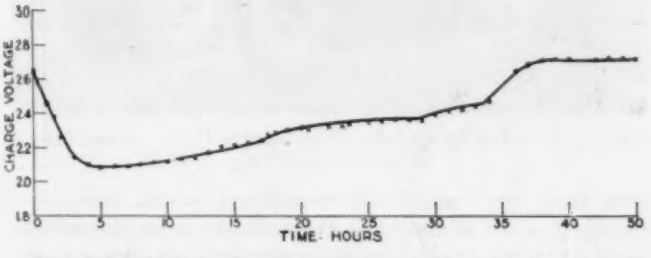


FIG. 3. Recharge voltage of a DD-5-1 cell at the 7.5 amp rate at room temperature. Recharge begun on an overdischarged cell with initial sp gr 1.022, final sp gr 1.300.

FIG. 4. Construction features of a DH-5-1 cell

[1] Willard Storage Battery Company, Cleveland, Ohio.

lead for grids in place of antimony-lead alloys normally used. The more common type of lead-acid batteries are made with grids containing 6–11 per cent antimony in the grid alloy. This causes the major handicap to the use of such cells in many applications because of their self-discharge, which amounts to approximately 1 per cent per day at 80°F (2).

Low Discharge (LD) cells lose not more than 15 per cent of their capacity per year. This is achieved by the use of pure lead grids which, in turn, influenced the design of these grids to the so-called mass type. Because they are made of

FIG. 5. Low Discharge cells. [The ruler is 18 in. (46 cm) long.]

pure lead, they are difficult to cast and handle. Because of the very nature of their use, the multiple plate construction required to provide high rates is not necessary. Plates, therefore, are from approximately 5/8 in. to 1 in. thick and number from 2 to 5 per cell, even in the 600 amp-hr (Fig. 4 and 5).

These cells were intended to serve as a source of power over long periods of time, and, therefore, at comparatively low rates of discharge. The design also involves a high ratio of active material to grid weight (1.75) compared to standard S.L.I. design (1.30). A high utilization of active material is attained by an ample acid supply.

Another result of operating at low rates of discharge the steady voltage which these cells deliver, and which d clines at extremely low rates.

Low rates, however, are not the exclusive field of applic tions for these cells, for they may be discharged at any ra for correspondingly shorter time during which their volta remains above the service requirement. No harm resul from such use of these cells.

As a result of these characteristics, the LD cells have fou numerous applications. They are used chiefly as isolat sources of power in buoys, channel markers, railway signa highway warnings, telephone and telegraph service, fire- a burglar-alarm systems of both open- and closed-circuit type range lights, aviation field markers and beacons, oil circu breakers, electric fences, etc. They are ideally suited source of power for various types of instruments both f industrial and laboratory service, especially in potentiom ters of indicating, recording, and controlling types.

It is general practice to use a size which will serve a perio of six months to one year between recharges, and, in genera to recharge the cells once per year. This helps preserve th cells in good health. Life is good in respect to time of servic under these conditions, 10 to 20 cycles being expected de pending upon the frequency and care of recharges.

There are three types of plates designed for the DA, DD and DH types of cells. The DA plates are used in only on 30 amp-hr two-plate cell. The DD plates are used in 11 amp-hr and 220 amp-hr three-cell batteries and a 220 amp-h two-volt cell, and the DH plates are used in 600 amp-h cells of two designs, one which has a deeper container an uses a special nonspill vent plug for buoy service.

Pertinent data are given in Table I. Electrical characte istics are given in capacity graphs and discharge and recharg curves, (Fig. 1, 2, and 3) and the general construction i shown in the photographs (Fig. 4 and 5).

REFERENCES

1. C. C. ROSE AND A. C. ZACHLIN, *Trans. Electrochem. Soc.*, **68**, 273 (1935).
2. A. C. ZACHLIN, *Trans. Electrochem. Soc.*, **92**, 259 (1947).

The Edison Nickel-Iron-Alkaline Cell

Fayette C. Anderson[1]

Historical

Approximately 40 years after the invention of the first practical storage battery by Planté, a patent was issued to Thomas A. Edison for a secondary cell with a nickel-iron couple in an alkaline electrolyte. The positive active mass of this cell consisted of oxides of nickel mixed with graphite and the negative active mass was a mixture of iron and iron oxide, also with graphite. These materials were enclosed in rectangular pockets made from thin, perforated sheet steel, which were attached to steel frames to form the positive and negative electrodes, respectively. The cell made by assembling these electrodes into a welded steel container, with an electrolyte consisting of an aqueous solution of potassium hydroxide, was known as the type "E" cell.

This type of cell was found to have certain structural weaknesses which caused its withdrawal from the market in 1904. Chief among these was the difficulty of maintaining the dimensional stability of the positive elements because of the volumetric changes which take place during the charge and discharge reactions. During the four years following 1904 these problems were given intensive study, and one by one they were solved. In 1908 the Edison cell with a tubular type positive, and essentially in its present form, was once again offered for commercial application.

Construction

The positive plates of the present-day Edison cell are made by clamping into a nickel-plated sheet-steel framework the tubes which contain the nickel oxide active material. These tubes are formed of perforated nickel-plated steel ribbon spirally wound on mandrels, and have locked seams. They are 1/4 in. in diameter and are made in several lengths

[1] Thomas A. Edison, Inc., Storage Battery Division, West Orange, New Jersey.

p to 4 inches. Each tube is reinforced by the addition of ight equally-spaced seamless steel rings. The active mate- al is introduced in small amounts and is tamped into place t a pressure of 2000 lb/in.^{2} Between the 300 layers of nickel- us hydroxide in each 4-in. tube are thinner layers of pure ickel flakes to give improved conductivity. These tubes have 5-hour rated capacity of 1.25 amp-hr and positive plates re rated in multiples of this value in accordance with the umber of tubes they contain. Thus the "B" type plate with 5 tubes has a normal rating of 18.75 amp-hr; the "D" type late with 60 tubes has a rating of 75 amp-hr.

The negative active material of the present Edison cell emains essentially a mixture of finely divided ferrous oxide nd metallic iron. Since the volumetric changes of the nega- ive active mass during cycling are insignificant it is feasible o use rectangular pockets, formed of perforated and nickel- lated steel ribbon, to contain this material. These pockets,

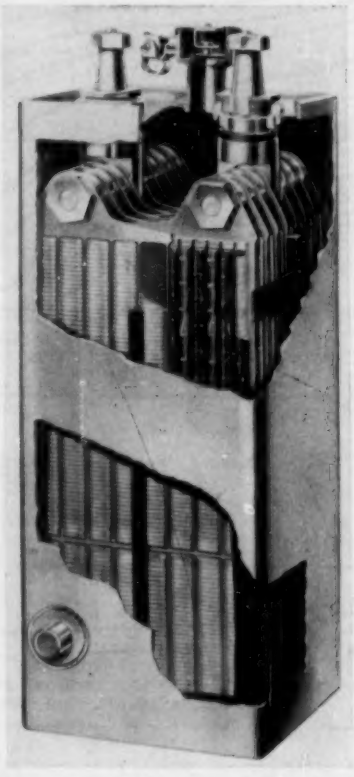


FIG. 1. Cutaway view of Edison cell with sectional views of a pocket and a tube.

each about ½ in. wide x 2⅞ in. long, are pressed into openings in a sheet-steel frame to make negative plates with capacities to match those of the positives.

A complete nickel-iron-alkaline cell contains one more negative than positive plate. Each plate group is assembled by bolting the selected number of elements to a steel pole, the base of the pole forming one of the separating members, or spacers. After intermeshing these groups, the adjacent positive and negative plates are insulated from each other by vertical hard-rubber pins, or rods, running their entire length. The edges of the plates are insulated from the bottom and from the sides of the container by grooved hard-rubber frames called grid separators.

The poles are tapered to fit the lugs of the intercell and intertray connectors. The connector lugs are steel forgings bored to fit the taper on the pole pieces and are swaged to heavy copper connecting links. The container is made of nickel-plated steel with all seams welded. Details of the construction and assembly are clearly indicated in the cut-away view shown as Fig. 1.

Electrochemical Reactions

The electrolyte of the Edison cell consists of an aqueous 21 per cent solution of potassium hydroxide to which has been added a small amount of lithium hydroxide.

It does not at any stage cause a disintegration or solution of the active materials. The normal density of the electrolyte in a new cell is about 1.21.

The exact mechanism of the electrode reactions is highly complex. During the passage of current through the cell in the direction of charge, the process at the negative or ferrous oxide electrode is the cathodic reduction of the ferrous oxide to metallic iron. The reaction at the positive or nickel-oxide electrode is the anodic oxidation of nickelous oxide to a higher oxide of nickel. On discharge, the reverse reactions take place with the production of useful electrical energy; the metallic iron (negative active material) is oxidized to ferrous oxide, and at the positive electrode the higher oxide of nickel is reduced to nickelous oxide. The electrolyte serves merely as a channel through which oxygen (or hydroxyl groups) are transferred to or from the electrodes. There is no significant difference in electrolyte concentration between the charged and discharged states, since concentration changes at one electrode are balanced (for all practical purposes) by opposing equivalent changes at the other electrode.

Battery Assembly

Edison cells are manufactured in a wide range of sizes and watt-hour capacities, all of which retain the basic design and construction features that were previously described. Different plate sizes and capacities are obtained by varying the number of tubes and pockets assembled, respectively, into the positive and negative grids. These plates are then combined in the desired numbers to obtain cells with watt-hour ratings from 13.5 to 1080.

Cells are assembled into batteries as needed to meet the voltage requirements of the equipment to be operated. For ease of handling, a group of cells is assembled into a painted hardwood tray by covering the suspension bosses with hard-rubber buttons which are then fitted into recesses provided in the tray slats or sides. This method of individually supporting the cells provides air spaces on all sides and adequately insulates the cells from each other.

In motive-power services, trays of cells are frequently assembled as a battery into a suitably fabricated steel cradle or box and provided with a polarized disconnecting plug so that the battery may be removed from the vehicle for charging. This makes it possible for an alternate battery to provide power for the vehicle thus keeping it in service for two or more shifts.

Operating Characteristics

Edison nickel-iron-alkaline cells are given a range of ratings to meet the requirements of their various applications. To serve as a reference point, however, the *normal* capacity rating arbitrarily assigned by the manufacturer, is based on the 5-hour discharge rate, and the *normal* charge consists of a 7-hour charge at the same rate. Other rates and periods of charge are possible but the normal charge is used as the standard whenever ratings are to be established or tests are to be conducted. It is a characteristic of Edison cells to develop at least 10 per cent more than the normal capacity rating to 1.0 volt at the 5-hour rate, within a short time after

they are installed in cycle services. Thus the amp-hr efficiency is about 80 per cent when based on a full charge and discharge but will run appreciably higher for partial cycles.

The cell voltages measured during a typical charge and discharge at normal rate and at room temperature are shown on the graph of Fig. 3. From these curves it will be noted that the average voltage over the discharge period is approximately 1.2 volts, and the average charge voltage is about 1.69 volts.

Characteristic discharge voltage curves for rates higher and lower than the normal value are shown in Fig. 4. These results illustrate the fact that practically full-rated capacity

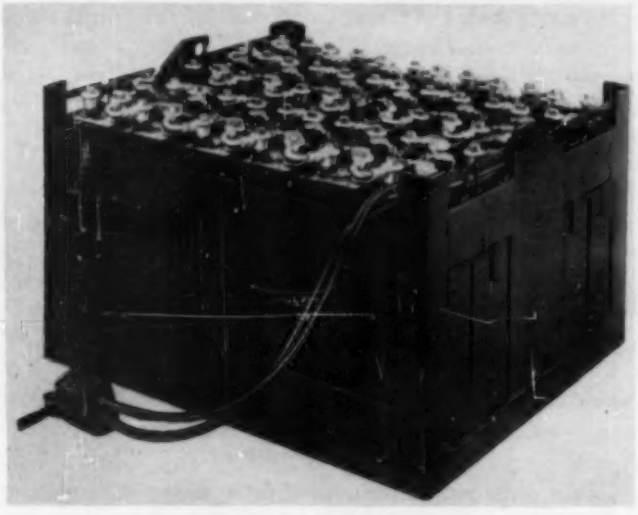


FIG. 2. Typical battery assembly (Cradle)

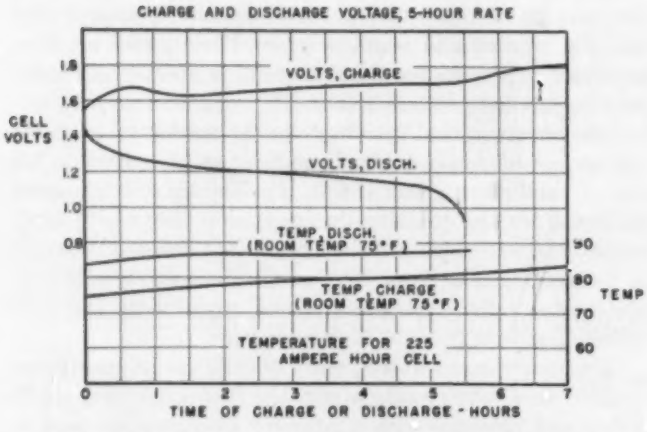

CHARGE AND DISCHARGE VOLTAGE, 5-HOUR RATE
VOLTS, CHARGE
VOLTS, DISCH.
TEMP. DISCH. (ROOM TEMP 75°F)
TEMP. CHARGE (ROOM TEMP 75°F)
TEMPERATURE FOR 225 AMPERE HOUR CELL
CELL VOLTS
TEMP
TIME OF CHARGE OR DISCHARGE - HOURS

FIG. 3. Cell volts and temperatures during charge and discharge.

can be obtained at rates up to several times the normal value because it is not necessary to impose a limit to the final voltage in order to avoid possible injury. In fact, the cells may be discharged to zero voltage without damage and accidental short-circuiting or charging in the reverse direction will not harm the elements.

The Edison nickel-iron-alkaline cell can be charged by any of the methods that are in common use. Representative cell voltages for a constant current charge were previously discussed and are shown in Fig. 3. Since this method requires frequent manual adjustment or elaborate automatic control equipment, the more common method for charging batteries in industrial services is that known as modified constant potential, or taper current charging. With this method, a fixed and permanent resistance is inserted in series with the ba[ttery], and no adjustments are made during charg[e]. A secon[d] advantage is that this method lends itself to practically auto[matic] charging since the charge can be terminated with [a] timer or amp-hr meter. The charging line must be capabl[e] of supplying a more or less constant bus voltage of at lea[st] 1.84 volts per cell, but higher voltages are more common[ly] used. The higher the bus voltage, the smaller will be th[e] taper of the charging rate and the more closely will it ap[-] proach the straight constant current method as a limit. Th[is] means that there will be less spread between the initial an[d]

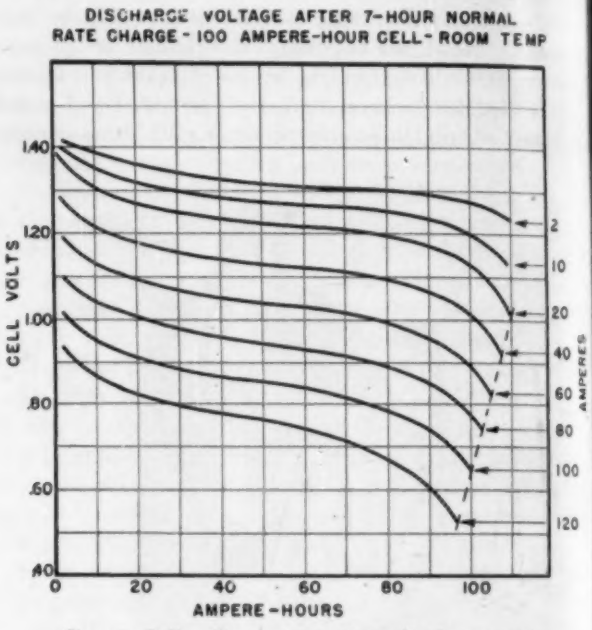


FIG. 4. Cell voltages at various discharge rates

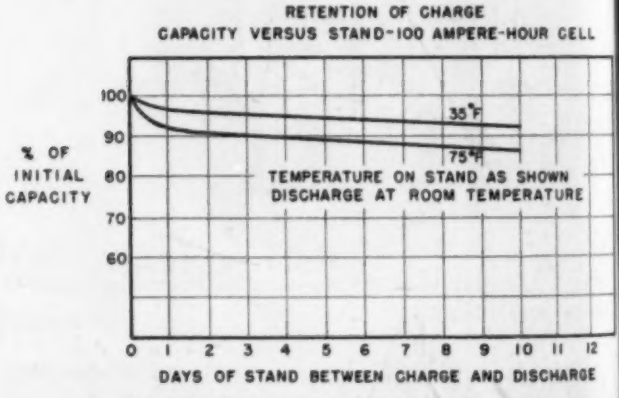

RETENTION OF CHARGE
CAPACITY VERSUS STAND - 100 AMPERE-HOUR CELL
% OF INITIAL CAPACITY
35°F
75°F
TEMPERATURE ON STAND AS SHOWN
DISCHARGE AT ROOM TEMPERATURE
DAYS OF STAND BETWEEN CHARGE AND DISCHARGE

FIG. 5. Capacity after charged stand

final current values, a factor of importance in the design and use of commercial charging equipment.

Edison nickel-iron-alkaline cells may be trickle-charged in services where the battery is used as a standby power source. The trickle-charge rate in amperes that must be furnished by the charging source is set at a value that will replace the idle-stand capacity losses. Recommended values for most applications may be calculated from the following equation:

$$\frac{\text{Rated amp-hr capacity} \times 0.16}{24}.$$

Higher values may safely be used, since the resulting overcharge will do no harm, and downward adjustments are recommended if excessive loss of water is noted. The voltage

t must be furnished to obtain these rates will range from
9 to 1.55 volts per cell at normal temperatures.

As with all electrochemical systems the reactions of storage teries are affected by their operating temperatures, and discussions of battery performance or life must take this tor into consideration. Longest life and best performance be obtained when the electrolyte temperature of Edison teries is maintained below the recommended maximum 115°F. Control of electrolyte temperatures can be readily ieved because of the air spaces provided on all sides of the

ABLE I. *Technical data: typical battery assemblies—cradle or demountable steel box*

	A8	C8	D8
ell type			
umber of cells	30	30	30
umber of trays	5	5	5
lls per tray	6	6	6
mp-hr capacity	300	450	600
att-hour capacity			
per Cell	360	540	720
per Battery	10,800	16,200	21,600
ength— Cradle	36.5 in.	36.5 in.	37.0 in.
Box	36.9 "	36.9 "	38.4 "
idth— Cradle	31.1 "	31.1 "	31.6 "
Box	31.5 "	31.5 "	31.9 "
eight— Cradle	17.0 "	22.0 "	29.0 "
Box	17.5 "	22.5 "	29.1 "
eight in pounds			
Single cell	28.0	40.9	54.8
Battery complete in cradle	1,001	1,140	1,953
Battery complete in box	1,114	1,602	2,130
ubic feet			
Single cell	0.213	0.298	0.407
Battery in cradle	11.15	14.45	19.56
Battery in box	11.78	15.15	20.62
ounds/ft³			
Single cell	131.3	136.9	135.0
Battery in cradle	89.8	99.5	99.8
Battery in box	94.6	105.8	103.2
att-hours/ft³			
Single cell	1,688	1,805	1,772
Battery in cradle	968	1,122	1,105
Battery in box	917	1,068	1,047
att-hours/lb			
Single cell	12.85	13.20	13.14
Battery in cradle	10.78	14.20	11.05
Battery in box	9.69	10.12	10.13

ndividually suspended cells, and because the steel container an excellent conductor of heat.

Under any given set of discharge conditions the capacity f the cell decreases as the electrolyte temperature drops ppreciably below 80°F. The extent of the decrease varies ith the rate of discharge, being (*a*) relatively small at low ates and larger at high rates, and (*b*) less when the discharge intermittent than when it is continuous. The wide applica- ion of nickel-iron cells to such services as motive power, ailway carlighting, signal, etc., is evidence that properly pplied batteries will give adequate reserve capacity at tem- eratures down to 0°F and below. At a temperature of pproximately −25°F, electrolyte of normal density will become slushy and crystallized but it will not freeze hard and cause mechanical injury.

When fully charged cells are permitted to stand idle there is a gradual loss of capacity. This loss is less at low storage temperatures as shown by the graphs of Fig. 5.

One of the advantages of nickel-iron cells is the ease with which they may be laid up for extended periods. This is chiefly of value in applications that are seasonal in nature, or where normal operations are curtailed for some reason or other. The recommended procedure for storing batteries of this type over long periods is to discharge them completely, short-circuit, and maintain the solution level above the plate tops. Heated storage is not required for there is no danger that they will be damaged by freezing.

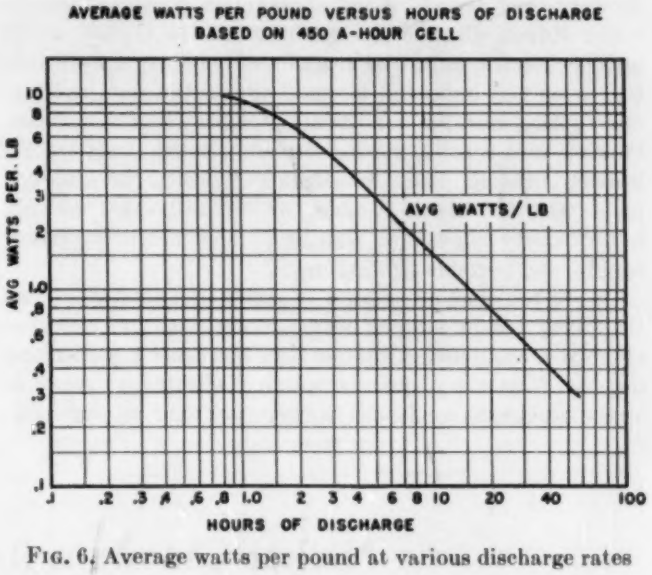

AVERAGE WATTS PER POUND VERSUS HOURS OF DISCHARGE
BASED ON 450 A-HOUR CELL
AVG WATTS PER LB
AVG WATTS/LB
HOURS OF DISCHARGE

FIG. 6. Average watts per pound at various discharge rates

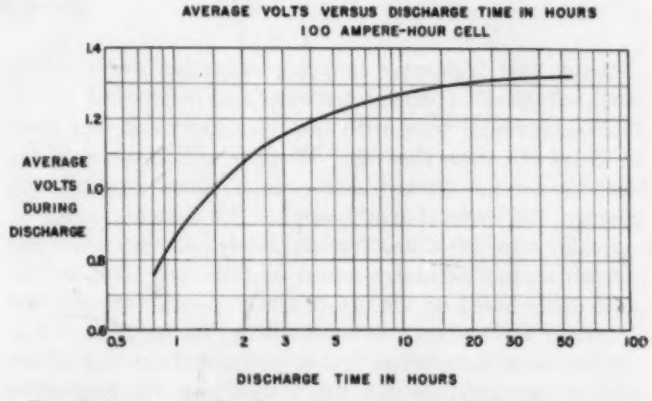

AVERAGE VOLTS VERSUS DISCHARGE TIME IN HOURS
100 AMPERE-HOUR CELL
AVERAGE VOLTS DURING DISCHARGE
DISCHARGE TIME IN HOURS

FIG. 7. Average cell voltages over a range of discharge rates

Engineering Data

The output of Edison batteries calculated in terms of watt-hours/lb or watt-hours/ft³ will vary somewhat with the size of the cell and the method of assembly. Values for three of the cell sizes that are used for many industrial applications and with assemblies in both cradles and steel boxes are shown in Table I. These are based on the rated outputs of the batteries, and are well below the results that would be obtained by using actual performance data.

By using the discharge data from test curves such as those shown on Fig. 7, and applying it to the type C8 cell, which weighs 40.9 lb and has a 5-hour rating of 450 amp-hr, the average watts/lb were calculated. These results were plotted

as ordinates, against the hours of discharge as abscissa on a log-log graph shown as Fig. 6.

The average cell voltages over a range of discharge rates are shown in Fig. 7.

Applications and Life

The nickel-iron-alkaline cell has been applied to almost every field in which storage batteries are used. Its steel construction and long life under severe operating conditions, even where neglect and abuse are encountered, make it particularly suitable for heavy-duty industrial and railway applications. The predominant feature of these services is that the battery is required to deliver its capacity over a period of one to eight hours as contrasted, for example, with the engine starting field which demands high current discharges for very brief periods. A list of the more important uses to which Edison alkaline storage batteries are applied would include: electric industrial trucks and tractors, storage battery mine and industrial locomotives, shuttle cars, railway-car lighting and air conditioning, railway signal systems, multiple unit control, marine services, electric street trucks isolated lighting plants, emergency lighting, time clocks, police and fire alarm systems, oil circuit-breaker control, miners safety-cap lamps, instrument and laboratory power supply, and portable lighting units.

One of the chief advantages of nickel-iron-alkaline cells is their long life in services where mechanical and electrical abuse is encountered. Vibration does not cause loss of active material from the plates nor are they affected by many of the accidental conditions of operation such as overcharging, overdischarging, short-circuiting, or reverse charge. The actual life in years will, of course, vary with the severity of the service. Average values will range from 7 years in heavy-duty services to recorded instances of 25 years or more in stand-by and floating applications.

GENERAL BIBLIOGRAPHY

Crennell and Lea, "Alkaline Accumulators," Longmans, Green & Co., New York (1928).

Lamar Lyndon, "Storage Battery Engineering," McGraw-Hill Book Co., Inc., New York (1911).

G. W. Vinal, "Storage Batteries," John Wiley & Sons, Inc., New York (1940).

Pender and Del Mar, "Electrical Engineers Handbook," 4th ed., Electric Power, John Wiley & Sons, Inc., New York (1949).

Thomas A. Edison, Inc., Storage Battery Division, West Orange, N. J., various publications.

A. E. Knowlton, "Standard Handbook for Electrical Engineers," 8th ed., McGraw-Hill Book Co., Inc., New York (1949).

E. F. Roeber, *Trans. Electrochem. Soc.*, **1**, 195 (1902).

A. E. Kennelly and S. E. Whiting, *Trans. Electrochem. Soc.*, **6**, 135 (1904).

M. de Kay Thompson and H. K. Richardson, *Trans. Electrochem. Soc.*, **7**, 95 (1905).

C. W. Bennett and H. N. Gilbert, *Trans. Electrochem. Soc.*, **23**, 359 (1913).

L. C. Turnock, *Trans. Electrochem. Soc.*, **30**, 273 (1916).

M. de Kay Thompson and L. R. Byrne, *Trans. Electrochem. Soc.*, **31**, 339 (1917).

L. C. Turnock, *Trans. Electrochem. Soc.*, **32**, 405 (1917).

Nickel-Cadmium Batteries—Pocket Type

Sven Bergstrom[1]

About 1890 Waldemar Jungner, a Swedish scientist, became interested in storage batteries and conducted extensive experimental tests with the types known at that time. At about the same time that Thomas A. Edison made his invention in the United States of a nickel-iron battery, Jungner had independently applied for patents covering approximately the same type of battery. Jungner then experimented further and received in 1901 and 1903 American patents based on the use of nickel oxide in the positive plates and iron and cadmium materials in the negative plates.

It was some years before this invention was put into a form suitable for industrial use, but a company was formed in Sweden which began to manufacture industrial batteries in 1910. From this small start, the business has grown until nickel-cadmium batteries are known and used the world over. Manufacture in the United States was begun in 1946.

The advantages of the nickel-cadmium battery are numerous. It is similar to the Edison battery in many important respects. Both are mechanically rugged, will withstand shock and vibration and are also electrically robust in that they will withstand overcharge, overdischarge, and standing idle in a discharged condition.

The advantages of the nickel-cadmium battery stem from the plate construction, the use of cadmium, and the use of an alkaline electrolyte. The cadmium metal used for the negative active material can be discharged at a high rate and at a low temperature. Although it does not give quite as high a discharge voltage as iron, it is stable on open circuit and shows very little self-discharge. It can be trickle-charged, and when standing idle it evolves practically no gas so that for some purposes nonspill cells are sealed, and need be vented to the air only during charge.

The positive plate of the cadmium battery is of a flat pocket type. This flat pocket construction allows extremely thin plates to be made and permits the plates to be brought close together. As a result, high voltages may be attained during high rate discharge and the battery can be used for Diesel cranking service.

Cell Construction

The pocket type of construction used for both positive and negative plates of the nickel-cadmium battery is similar to the pocket type negative used in the Edison battery. Pockets or compartments are fabricated from sheet steel which has been nickel-plated and pierced by many small holes. These pockets are approximately ½ in. x 5 in. in size, have a thickness which may be anywhere between 0.070 in. and 0.250 in. and are filled with active material. The active material of the positive plate is a highly purified grade of nickel oxide. During charge, this is converted to $Ni(OH)_3$, while during discharge, it is reduced to $Ni(OH)_2$. The active material also contains graphite flake which adds to the electrical conductivity. The negative plate consists of cadmium metal. During

[1] Nife, Inc., Copiague, New York.

harge, this cadmium is converted to cadmium hydroxide during charge is converted back to metallic cadmium. Plates are assembled from pocket elements in almost any ired size, and then these plates are collected into a cell h almost any desired number of plates per cell. In this y, capacities of 2 to 1000 amp-hr or more can be obtained.

Electrolyte

The electrolyte used in the various types of alkaline cells ubstantially the same. It is high purity potassium hyxide in water and may have, in addition, a small amount lithium hydroxide. The normal specific gravity is 1.190 , if cells are to operate in a cold climate, the specific vity may be increased to 1.23–1.30. The higher gravities

are shown for three different classes of battery. One type of battery is built for service where a low internal resistance is not required. It is for a battery containing fairly thick plates and meant to be used in stand-by service where it is required to deliver power for five hours or longer. At the 10-hour rate this battery, shown as line A in Fig. 1, produces more power per pound of battery than the other two types shown. At the 0.5-hour rate it produces less power. By going to thinner (line B) and still thinner (line C) plates, it is possible to improve the voltage so that at the $\frac{1}{10}$-hour discharge capacity, the power output reaches 25 watts/lb. This is done by sacrificing the power output at the 10-hour rate. Such a battery is obviously to be used primarily where a high rate discharge is required.

TABLE I. *Characteristics of nickel-cadmium pocket type storage batteries*

	Type AVC 3316				Type SAVC 3516				Type STN 4516			
-hr at 5-hr ate ..... ght, kg..... e, c.....	313 16.9 7700				306 17.3 7060				310 21.5 9900			
	% Cap.	Avg v	Whr/lb	W/lb	% Cap.	Avg v	Whr/lb	W/lb	% Cap.	Avg v	Whr/lb	W/lb
10	104	1.235	10.85	1.085	103.5	1.245	10.35	1.035	101.5	1.26	8.4	0.84
5	100	1.20	10.15	2.03	100	1.225	9.83	1.966	100	1.25	8.18	1.64
2	90	1.12	8.45	4.22	93	1.17	8.66	4.33	95	1.225	7.62	3.89
1	77	1.02	6.64	6.64	82.6	1.10	7.27	7.27	89	1.19	6.91	6.91
½	61.5	0.89	4.62	9.24	67.4	1.00	5.40	10.8	79.5	1.135	5.90	11.80
¼	—	—	—	—	51.4	0.875	3.61	14.44	66	1.045	4.51	18.04
⅙	—	—	—	—	43.3	0.79	2.74	16.44	56.4	0.98	3.61	21.66
1/12	—	—	—	—	31.0	0.61	1.515	18.2	39.6	0.865	2.24	25.9

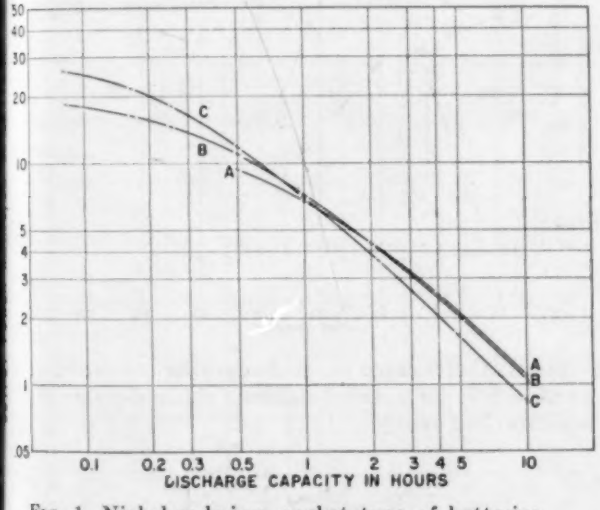


FIG. 1. Nickel-cadmium pocket type of batteries

ve better performance at subzero temperatures but shorten e life of the battery when used at normal temperatures. uring the operation of a battery, no potassium hydroxide or thium hydroxide is consumed so that the specific gravity es not change with the state of charge of the battery and e freezing point of the electrolyte is always quite low. he electrolyte never freezes solid so that no damage is used to the cells by freezing and they perform as usual ter being thawed out.

The effect of lithium hydroxide is believed to prolong the fe of the cell by making it more immune to electrical abuse.

Engineering Characteristics

The capacity of the storage battery as affected by the rate f discharge is shown in Table I and in Fig. 1. Three lines

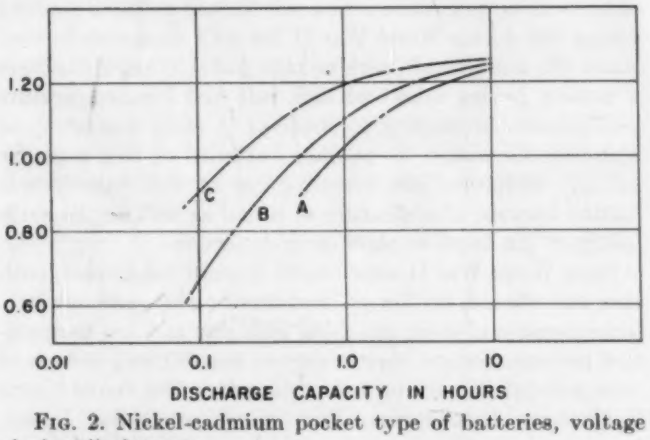


FIG. 2. Nickel-cadmium pocket type of batteries, voltage during discharge.

The voltage during discharge is shown in Fig. 2 for these same three classes of battery. At high rate discharge the voltage falls off on all batteries. The thinnest plate nickel-cadmium battery shown in this chart is considerably superior to the other two batteries over the entire range of useful discharge rates and obviously has its greatest advantage at high rate of discharge. The batteries used in calculating performance data for this chart are shown in Table I. These are approximately 300 amp-hr batteries and it is assumed, in general, that, since data are expressed in watts per pound of battery, the same data will apply to other sizes of battery.

The density of these batteries is approximately 135 lb/ft³. Some cells are also made with a larger electrolyte volume above the plates and, therefore, have a lower density.

Self-Discharge

Because of the cadmium negative-active material, the self-discharge of these batteries is quite low. Where extreme care

is taken with the purity of materials, a self-discharge rate of 20 per cent per year or less has been attained. Many commercial batteries will fall between 20 and 40 per cent per year of self-discharge. The effect of temperature on these batteries is somewhat different from other batteries. The nickel-cadmium battery can be used for high rate discharge at low temperature, and its performance in this kind of service expressed per pound of battery will be close to that of a motive power type lead-acid battery and will be considerably superior to an Edison battery. At high temperatures, the life of the battery on overcharge is excellent although the manufacturers recommend that the battery temperature be not allowed to exceed 115°F.

The life of the battery under service conditions is good. Instances are on record of batteries in continuous service for over 25 years in Europe. The American-made batteries have not been on the market long enough to establish such an enviable record, but there is no reason to believe that they will be inferior to European batteries in this respect. For automobile use, the French manufacturer guarantees [illegible] battery for four years.

Usefulness

In view of the above engineering charact[illegible]istics, it is surprising to find that a nickel-cadmium [illegible]attery can be [illegible] as a replacement for practically any [illegible]ther type of batt[illegible] limited solely by cost and a slight difference in weight [illegible] volume. It has not yet found extensive usefulness for a[illegible] mobile starting because it occupies about one-third m[illegible] space and the cost is very considerably higher than a [illegible] battery. In the industrial field, however, it has attained wide usefulness for stand-by and emergency lighting, Diesel cranking, for telephone service, for railroad carlight service, and, to a limited extent, for electric truck operati[illegible]

Although the sales volume of the battery at present is as great as that of other types of storage battery, it is pected that the nickel-cadmium battery will become an creasingly important commercial article in the United Sta[illegible]

Sintered Plate Nickel-Cadmium Batteries

G. B. Ellis[1], *H. Mandel*[1], *and D. Linden*[1]

The nickel-cadmium battery has been known since about 1900 and has been constructed for many years in the familiar tubular and flat pocket designs. In the last fifteen years, however, the sintered plate battery has been developed. The early work on this construction was limited to thick sintered plates, but during World War II the AFA Company in Germany did considerable work on thin plates in order to obtain a battery having improved high rate and low temperature performance for starting applications. A plant was set up at Hanover, Germany, to produce batteries of this type for military purposes, but extensive use of this battery was limited because of a shortage of nickel as well as the early failure of the negative plate on cycle service.

Since World War II considerable interest has existed, both here and abroad, in thin plate sintered nickel-cadmium batteries because of their promising high rate and low temperature performance and their ability to float for long periods of time without damage or loss of capacity. The Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey, has sponsored this development within the United States which has resulted in the establishment in this country of the "know how" and the facilities for the fabrication of nickel-cadmium batteries which have successfully fulfilled the power requirements of several special military applications.

The sintered plate battery uses nickel oxide as the positive active material and cadmium metal as the negative active material, but differs from other nickel-cadmium batteries in the method of support. Plates are made from nickel powder which is molded into shape and heated at an elevated temperature in a nonoxidizing atmosphere. This gives a strong, porous plate which contains about 80 per cent pore volume.

Active material is then impregnated in the pores of these plates by soaking them in a solution of nickel salts to make positive plates, and a solution of cadmium salts to make negative plates. Details of the process have been described by Fleischer (1).

Performance measurements were made on a group of 5-

[1] Power Sources Branch, Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.

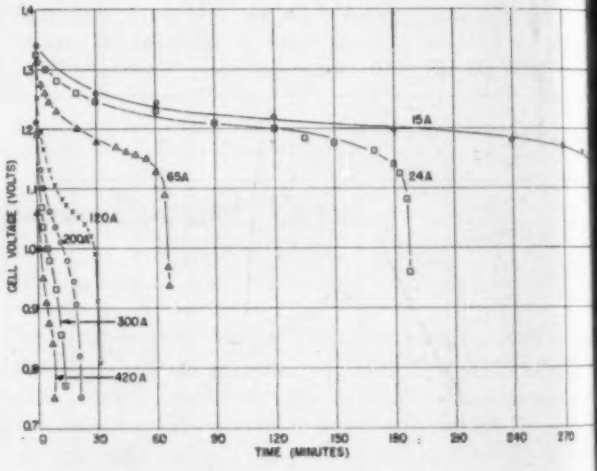


FIG. 1. Cell voltage vs. discharge time, all discharge ra[illegible] at 85 ± 5°F, for a nickel-cadmium sintered-plate cell, ra[illegible] capacity: 75.0 amp-hr.

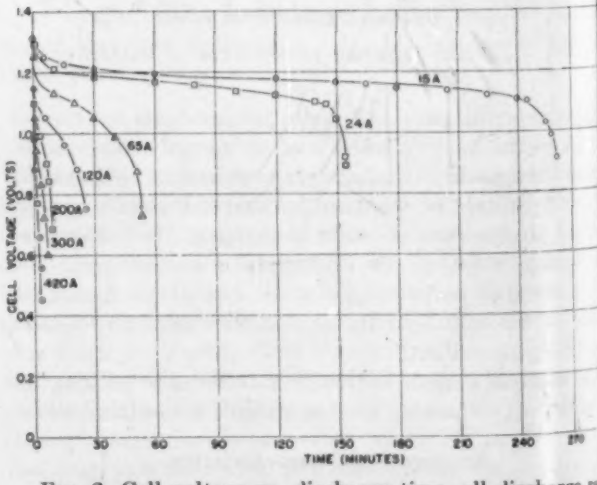


FIG. 2. Cell voltage vs. discharge time, all discharge ra[illegible] at 0°F, for a nickel-cadmium sintered-plate cell, rated capaci[illegible] 75.0 amp-hr.

batteries rated at 75 amp-hr. The average battery had a ght of 41.5 lb, and a volume, excluding the terminals, 45 in.³ It actually delivered 415 whr at the 5-hr rate. s can be expressed as 10 whr/lb, 1311 whr/ft³, and gives ensity of 131 lb/ft³.

The characteristics of the sintered-plate nickel-cadmium ttery can best be illustrated by the curves in the following ures.

Discharge curves.—Curves in Fig. 1–4 are voltage vs. e curves for various discharge rates at temperatures from F to −65°F. In establishing these curves, charging was e overnight for 16 hours at 85°F ±5°F at constant current.

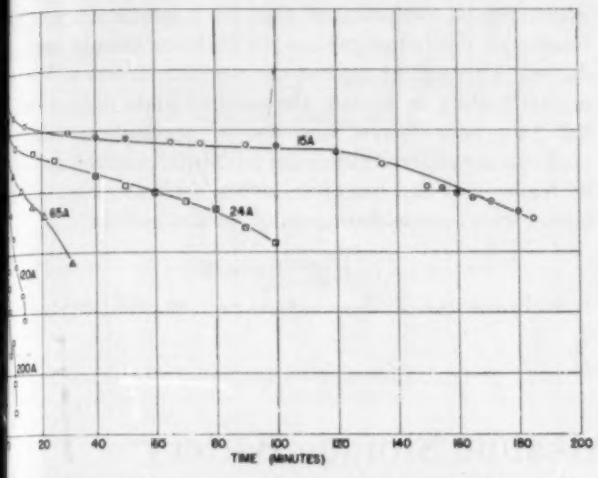


FIG. 3. Cell voltage vs. discharge time, all discharge rates −40°F, for a nickel-cadmium sintered-plate cell, rated pacity: 75.0 amp-hr.

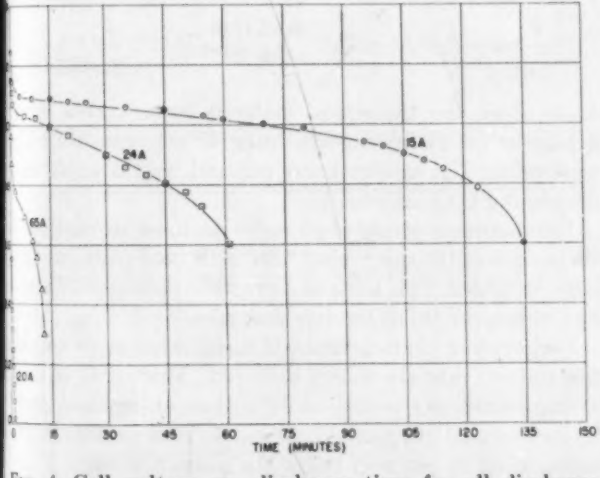


FIG. 4. Cell voltage vs. discharge time for all discharge tes at −65°F for a nickel-cadmium sintered-plate cell, rated pacity: 75.0 amp-hr.

The charge rate was determined so that the ampere-hour put would be equal to the ampere-hour capacity withdrawn the preceding discharge plus 60 per cent of the rated cell pacity. Though it was recognized that the overcharge robably was more than necessary, this procedure was fol-wed to be consistent with that generally recommended for ocket-type batteries in order to obtain comparable test ata.

Relative capacities vs. temperature and discharge rate.—The urve in Fig. 5 shows the relationship between discharge ate in minutes and the ampere-hour capacity obtained at he various temperatures for the sintered plate cells. The capacities are measured as a percentage of the ampere-hour capacity obtained at the five-hour rate at 80°F. It should be noted that at 80°F the capacity at the one-hour rate is still 93 per cent with the sharp break in the curve occurring at about the fifteen-minute rate. As the temperature is decreased the capacity falls off more rapidly and the break in the curves occurs at lower rates, i.e., higher hourly rates.

Relative watt-hour capacities vs. temperature and discharge rate.—The curve in Fig. 6 is a curve of watt-hour capacity plotted against discharge rate at various temperatures for the sintered-plate cell. These capacities are plotted as percentages of the watt-hour capacity obtained at the five-hour

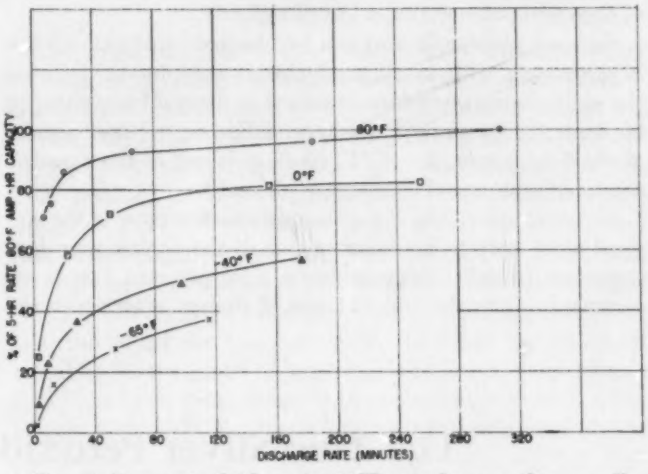


FIG. 5. Per cent of 5-hr rate, 80°F amp-hr capacity, vs. discharge rate (min) for a nickel-cadmium sintered-plate cell, rated capacity: 75.0 amp-hr.

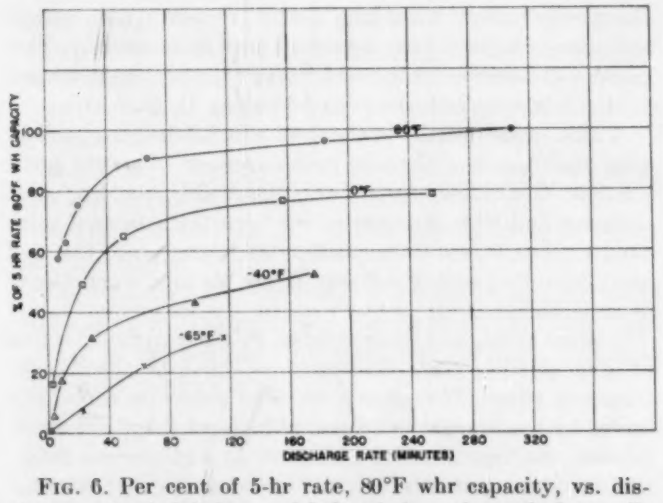


FIG. 6. Per cent of 5-hr rate, 80°F whr capacity, vs. discharge rate (min) for a nickel-cadmium sintered-plate cell, rated capacity: 75.0 amp-hr.

rate at 80°F, as was done for the ampere-hour capacities. The midpoint discharge voltages, which were the cutoff voltages plus 0.15 volts, were used to calculate the watt-hour capacities. The cutoff voltages, in turn, were determined by taking a drop of 0.3 volt from the cell voltage after 10 per cent of the total discharge time to that cutoff voltage had elapsed. These curves have a greater slope than the ampere-hour capacity curves because the midpoint voltages are lower than one (1) volt at the higher rates and lower temperatures and higher at the other discharge conditions.

Charging characteristics.—Sintered plate nickel-cadmium batteries can be charged successfully by either constant cur-

rent or constant potential methods. The end-of-charge potential for constant current charging is generally lower than that for the pocket type of batteries. The charging efficiency, too, is higher for the sintered plate battery in that charging can be accomplished with an input-output ratio of 1.2. Pocket type batteries generally require a ratio of 1.4 to 1.6.

Overcharging has no detrimental effect on the performance of the sintered-plate battery and actually results in an increase in the capacity on the succeeding cycle primarily due to the formation of increased amounts of the higher oxides of nickel.

The sintered plate nickel-cadmium cells, like other nickel-cadmium cells, can be successfully floated for extended periods of time without suffering a loss of capacity.

Sintered plate cells also can be charged at extremely low temperatures with fairly good charge acceptance, utilizing the same charge procedure as is used at normal temperatures; for example, on an 80°F discharge following a 7-hour charge at the 5-hour rate at −40°F, 50–60 per cent of the capacity available after an 80°F charge is obtained.

Self-discharge.—The self-discharge characteristic of the sintered-plate battery is similar to that of the pocket-type construction. Initially, approximately a 10 per cent loss is experienced during the first 48 hours of storage, after which the loss tapers off to approximately 3 per cent per month a the first month. This results in a capacity loss of about 50 cent during the first year of storage at normal temperatu

Life.—Cycle service up to 700–1000 cycles has been ported for sintered-plate nickel-cadmium batteries. In s instances of battery cycling and of controlled cycling negative plates, a gradual loss of negative plate capacity been observed. This condition is currently being investiga to determine the cause for this capacity loss and to deve means for overcoming it.

The sintered plate nickel-cadmium battery has cert promising performance characteristics which offer advanta for certain applications and establish the desirability of furt improving its performance through a continuation and tension of the investigations which have already been c ducted. Although at present the commercial and military of this battery is limited, the sintered plate battery will, the very near future, find use in applications where performance characteristics are particularly suited and wh its higher cost and use of materials, such as nickel and c mium, which are in short supply, can be justified

REFERENCE

1. A. Fleischer, *J. Electrochem. Soc.*, **94**, 289 (1948).

The Zinc-Silver Peroxide-Alkaline Storage Battery

Samuel Eidensohn[1]

The use of silver oxide as the cathodic material in a rechargeable battery has a long history. However, no practical cell appears to have been developed until quite recently. This paper will describe the type of storage battery characterized by the following features as developed by H. G. Andre.

A zinc anode, usually in the form of a porous plate, undergoes oxidation to zinc oxide in the presence of a very small amount of alkaline electrolyte. Presumably the zinc first dissolves and then precipitates out from the saturated solution. Constructional design minimizes migration of the zinc away from the point of solution. Hence the zinc is considered as an insoluble anode.

A silver peroxide cathode, formed by electrolytic oxidation of silver or silver oxide, undergoes reduction to silver oxide, thence to silver. This gives a two-step reduction curve, observed at low current densities, with about 0.3 v difference between the maximum for each step. At high current densities, the higher potential is not observed as the electrochemical reduction of silver peroxide to silver oxide becomes polarized to the potential of the silver oxide. The actual cathodic potential depends on the equilibrium between silver peroxide, silver oxide, and silver present in the cathode.

The electrolyte is an aqueous solution of KOH which is saturated with respect to zinc oxide.

The plate separation in this type of cell takes the form of a nonwaterproof cellophane bag in which the cathode is completely wrapped. Other separator materials may be used in conjunction with the cellophane.

On charge, the discharge reactions are reversed with very high efficiency. The charge voltage also exhibits the stepwise aspect of the oxidation of the positive plate.

[1] Battery Section, Bureau of Ships, Department of the Navy, Washington, D. C.

The over-all electrochemical reaction may be written

$$Ag_2O_2 + H_2O + 2Zn \underset{\text{charge}}{\overset{\text{discharge}}{}} 2Ag + ZnO + Zn(OH)_2$$

from which the theoretical material requirements are 3. g/amp-hr (.0084 lb/amp-hr), using 40 per cent KOH as t electrolyte. The ampere-hours per unit weight would be 2 amp-hr/kg (119 amp-hr/lb).

In practice an excess of all materials must be provided a the weight of the case, cover, terminals, and plate conduct must be added. This leads to a practical output of 77 amp-h kg (35 amp-hr/lb) at the ten-hour rate.

Performance characteristics of a cell rated at 40 amp-hr the 10-hour rate are shown in Fig. 1. This curve shows t average watts per pound, at 80°F, and at constant curre plotted against the time of discharge. End voltage has be taken to be 10 per cent below the plateau voltage. This c weighs 1.46 lb and occupies 25 in.³, excluding the cell term nals. To convert watts per pound to watts per cubic fo multiply by 101. A typical low rate discharge and charg curve is shown in Fig. 2. The discharge rate was 5 amp an the charge rate was 2 amp. Discharge curves at high rat are shown on Fig. 3.

Self-Discharge

The effects of stand in the filled and charged conditio produce a reduction in capacity on subsequent discharg Present opinion is that these effects are greatly influenced b the amount of water in the cell. Drying out of the cell an exposure of the components to air are major factors in th deterioration of the cell. These factors were not appreciate until recently, thereby vitiating most of the available sel discharge data.

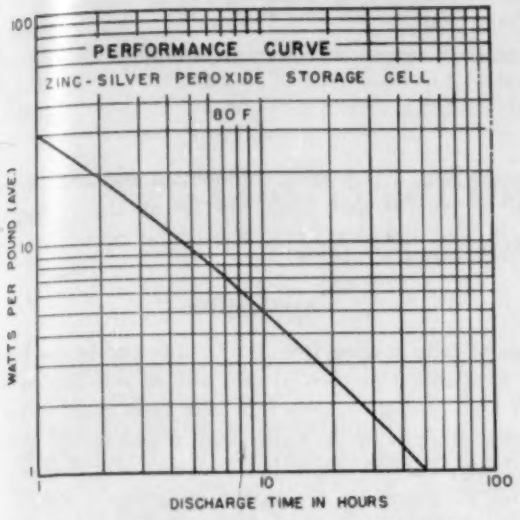


FIG. 1. Watts/lb vs. discharge time (hr)

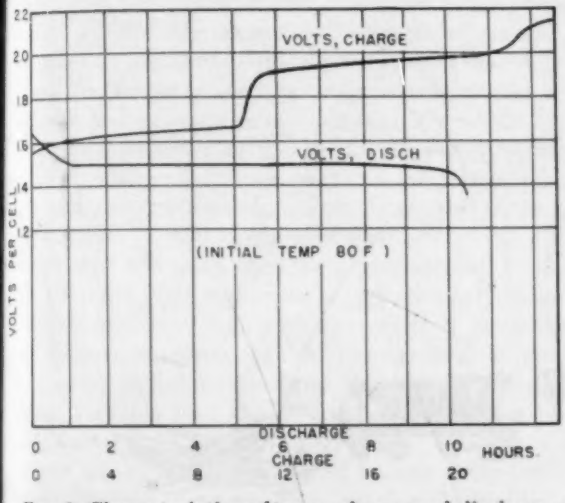


FIG. 2. Characteristic voltages, charge and discharge

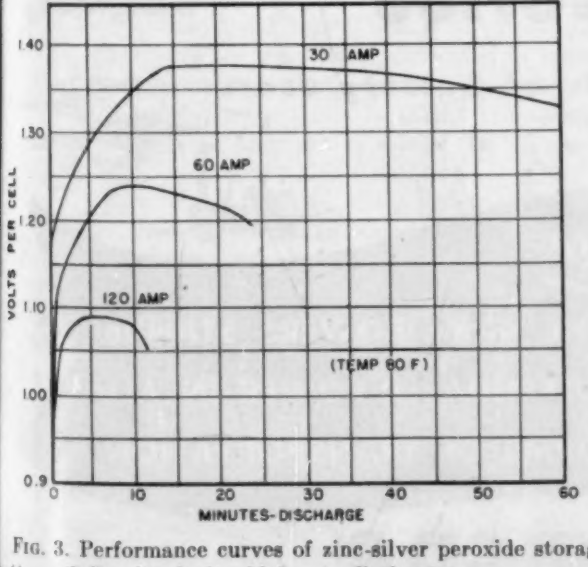


FIG. 3. Performance curves of zinc-silver peroxide storage battery. Cell volts during high rate discharges.

Results of tests with no control of electrolyte content, are reasonably consistent over a 30-day period, at 80°F. Very slight loss, averaging about 3 per cent, has been observed. For longer periods, the data is increasingly inconsistent. For a 60-day stand at 80°F, about 33 per cent loss has been reported; 90-day, about 50 per cent loss.

However, with protection against air exposure, test cells have given 48-weeks stand with 77 per cent charge retention. Similar cells, with no protection, dropped to 50 per cent in about 9 weeks.

At higher temperatures the effect of stand is accelerated. Tests with control of electrolyte content have not yet been reported. Tests with no control of electrolyte indicate that at 50°C (122°F) the loss of capacity in 14 days is about 30 per cent. Complete failure has been reported after 92 hr at 75°C (167°F).

Life

The life of the present zinc-silver peroxide storage battery depends on the design as well as the service in which the cell is employed. Cells designed for very high power output will endure only 5–10 high power cycles. This is probably caused by the very high temperatures produced within the cell. Cells designed for moderate rates and cycled at about 2 days per cycle have given more than 90 cycles. Indications are that several hundred cycles may be obtainable on the basis of increasing knowledge of the causes of cell deterioration.

Since deterioration takes place while the charged cells are idle, the longer the time per cycle, the fewer the cycles obtainable. Thus a group of cells, capable of over 60 cycles on a 2 day per cycle basis, dropped to about 80 per cent of rating in only 6 cycles in the course of which the cells were idle for 180 days.

On the other hand, an interposition of a stand in the discharged condition for 6 months did not appreciably affect the number of cycles obtained.

Floating the cells has been done under the following conditions:

Two cycles at the 1-hour rate ending in the fully charged condition followed by

30-day float at 1.90, 1.95, 2.00 v per cell cycle at 1-hour rate plus charge followed by

60-day float at 1.90, 1.95, 2.00 v per cell cycle at 1-hour rate plus charge followed by

90-day float at 1.90, 1.95, 2.00 v per cell cycle at 1-hour rate plus charge.

No watering was done and no protection against water loss was given. Taking the average capacity on cycle 1 and cycle 2 as 100 per cent, the relationship between float time and cell capacity was as follows:

	% Capacity after float		
Float time (days)	30	60	90
Float volts			
1.90	94	68	32
1.95	132	127	110
2.00	123	130	117

It will be noted that the cells were actually floated for 180 days. It is possible that an uninterrupted float for the same periods indicated would give quite different results.

The effect of overcharge on life is not well determined. Excessive overcharge is detrimental to life, whereas undercharge will cause a decline in capacity. The optimum overcharge is possibly about 10 per cent.

Cells have been subjected to temperatures below minus 78°C with no adverse effects noted after heating to 50°C.

Condition of Shipment

Cells are normally shipped filled and formed but in the discharged condition. They should be put in service within six months after receipt and kept in a cool location during the storage period. It may be necessary to add water when giving the first charge. Longer storage periods may be possible after more experience has been accumulated on protection against water loss.

It is anticipated that shipment in the dry condition will be feasible. This may make the storage life indefinite.

Outstanding Characteristics

The outstanding characteristic of this storage battery is the high output per unit weight and space. Fig. 3 permits the calculation that the energy output per pound is 50 whr at the 10-hour rate and 30 whr at the one-hour rate. More recently, the cell on which Fig. 3 is based has been improved by 50 per cent with no change in volume and with an increase of 20 per cent in weight. This gives a unit output as follows:

	Whr/lb	Whr/ft³
10-hour	62.5	7500
1-hour	37.5	4500

In comparison, a very good commercial lead cell will deli about 17 whr/lb and 2260 whr/ft³ at the 10-hour r 9 whr/lb and 1200 whr/ft³ at the 1-hour rate.

Availability

Sizes of cells ranging from 0.5 to 100 amp-hr are comm cially available. Commercial uses are, as yet, limited by rather high cost of the cells but have been found in porta electrical equipment in which cost is secondary to ene availability. Foreign use includes miner's lamp batteries portable photographic equipment. Progress in reducing and lengthening life will undoubtedly extend the field commercial use for this type of battery.

Feature Section

The Teaching of Electrochemistry

The Electrochemical Society Round-Table Discussion[1]

R. B. Mears[2]

Before discussing electrochemical education it is well to consider the need in industry for men trained in electrochemistry. A committee appointed by the Board of Directors of the Society in 1949 has conducted a survey to determine the need for electrochemists in industry The findings of this committee have been summarized during this discussion by Dr. R. M. Hunter. However, to obtain a direct idea of industry's belief regarding the need for electrochemists, I have conducted a small survey of my own in the Pittsburgh district. I asked the Personnel Directors of several large companies in the Pittsburgh area if they were at present looking for people trained in electrochemistry and if they had ever had requests from their plants or mills for men trained in electrochemistry. The answer was "no" to both questions. Generally the research organizations of these companies had or were seeking electrochemists but the plants or mills never or rarely requested them.

From this it appears that the expressed need for electrochemists is not large but, as we in our laboratory know from personal experience, even with the relatively small demand it is difficult to obtain men who are trained in this field. The number of people having electrochemical training who became available from the colleges each year must be very small, indeed.

There are, thus, two facts that become immediately apparent: (1) the expressed demand for electrochemists is small, and (2) the supply of trained electrochemists is even smaller than the demand.

What can be done about this? There is at present little value in attempting an educational campaign to interest industry in employing more electrochemists. The immediate need is to interest more students in taking some electrochemical courses while they are in college. This campaign should probably begin at the high school level.

Faced with a related problem, the American Society for Metals some years ago started an intensive campaign in the high schools to interest people in metallurgy. The first step by the A.S.M. was the appointment of an Advisory Committee on Metallurgical Education, under the Chairmanship of Dr. R. F. Mehl. This committee worked out a broad plan. One of their first acts was the preparation of a short brochure entitled "A Career in Metallurgy." This brochure was aimed at giving high school students sufficient information on metallurgy as a career so that they might at least consider it further. A larger booklet entitled "Your Career in the Metallurgical Profession" was also prepared. In the 96 pages of this booklet, the demand for metallurgists, the nature of metallurgical work, and the careers of several metallurgists are discussed.

After these publications were prepared, local committees of each chapter of A.S.M. were organized. Each member of these local committees was assigned to one high school in his vicinity. Armed with the literature mentioned above, the A.S.M. contact man then called on the vocational guidance counselor of the school and offered to supply any information on metallurgy the counselor might require.

The A.S.M. contact man was prepared to supply booklets, arrange to show films on the metallurgical industries, provide a speaker to tell groups of students about metallurgy or arrange for inspection trips of metallurgical plants or laboratories.

It seems to me that such a procedure is certain to increase interest in metallurgy as a career.

Chemical engineers also have not been indifferent to the situation. W. T. Nichols[3] reports the results of a survey made with the cooperation of the 94 student chapters of the American Institute of Chemical Engineers. Professors in colleges and men in industry were asked, "How can industry and colleges cooperate better to improve chemical engineering education"?

A summary of the replies to this question is given in Nichols' paper. Any individual interested in electrochemical education can find valuable suggestions in the Nichols article.

Nichols also discusses the initiation of a senior course in plant design at Washington University in St. Louis. This 3-hour-a-week course is taught for a full semester almost entirely by chemical engineers from industries in the St. Louis area. It is a credit course with examinations being given by the faculty members.

This course has greatly increased a feeling of cooperation between industry and colleges in the St. Louis area. It has given senior college students a closer contact with industrial problems and has given the lecturers an opportunity of sizing up potential chemical engineering employees.

In some areas, similar arrangements could be made for courses in electrochemistry. The short courses in corrosion that have been sponsored in various colleges by the National Association of Corrosion Engineers have increased interest in corrosion research. Possibly similar courses could be arranged in electrochemistry.

Other procedures include the sponsoring by The Electrochemical Society and interested industries of electrochemical exhibits. The exhibits might be prepared by high school or college students with prizes for the winners.

Annually in Pittsburgh, such an exhibition is held at the Buhl Planetarium with prizes for exhibits in Chemistry, Engineering, Physics, and Biology. There is no special prize in Electrochemistry.

Similarly, awards or scholarships for technical papers in electrochemistry at both undergraduate and graduate levels

[1] This discussion took place at the Philadelphia meeting on May 5, 1952.

[2] Research and Development Laboratory, United States Steel Company, Pittsburgh, Pennsylvania.

[3] W. T. Nichols, *Chem. Eng. Progress*, **48**, 201, 1952.

in colleges would be helpful. If each local section of the ECS sponsored one or more such awards in the colleges in its vicinity, interest in electrochemistry would be increased.

One of the best ways of increasing interest in electrochemistry is also the most painless. Many laboratories and plants employ extra summer help. The summer employment of high school juniors, seniors, and science teachers, as assistants in electrochemical work can greatly increase their knowledge of, and interest in electrochemistry. Similarly, the summer employment of college students and teachers is also valuable.

In the above, I have touched briefly on (1) developing a recognized need for electrochemists, and (2) interesting high school and college students in electrochemistry.

The next problem is what to teach!

It seems doubtful to me if a curriculum in electrochemistry or in electrochemical engineering is needed. Instead, I believe that undergraduates at the junior and senior level should be permitted to elect special courses in electrochemistry. This will raise the immediate outcry that the standard technical curricula are already so crowded that it would be impossible to squeeze anything else in and undesirable to drop any course from the curricula to make room for one in electrochemistry. Actually, rigid requirements of many curricula are of questionable value to the student, although it may ease the work of committees that attempt to accredit such curricula. Looking around our own laboratory, it appears that we do not really need any two men who have had exactly the same technical background.

We need one metallurgist who has specialized in physi another who has a special training in mechanical engineerin another who has had extra courses in statistics, and anoth who has had some *electrochemistry*. We would value the la named metallurgist even though he were deficient in so other field that is normally specified in the metallurgi engineering curriculum.

The same is true of electrical engineers, chemical engineer chemists, and physicists. We would be glad to have at le one of each of these who had some extra training in electr chemistry, even if he were deficient in one of the convention subjects on the curriculum.

The main points of this discussion may be summed up a follows:

1. The recognized need for electrochemists is only a fra tion of the potential demand.

2. Even in this situation, men with training in electr chemistry are in short supply.

3. To increase the supply of electrochemists, an educationa campaign reaching the high schools as well as the college is needed.

4. The summer employment of students and teachers fro high schools and colleges as assistants in electrochemica work at plants or research laboratories is a convenient wa of interesting more people in electrochemistry.

5. Rigid curriculum requirements are of questionable valu to industry. Some departure from a rigid set of courses t permit each student a certain latitude in selecting a mino field of specialization is desirable.

The Electrochemical Society

Montreal Meeting

October 26, 27, 28, 29, and 30, 1952

Sessions on

Battery, Corrosion, Electric Insulation, Electrodeposition, Industrial Electrolytic

Headquarters at the Sheraton-Mount Royal Hotel

Plant Trips and Other Plans for Montreal Meeting

Arrangements have now been completed for members and guests attending the 102nd meeting of the Society in Montreal, for two plant trips, within the city, scheduled for Tuesday and Wednesday afternoon, October 28 and 29. The first of these is a visit to two of the laboratories of McGill University, and the other is to two of Montreal's most interesting installations, the Canadian Copper Refiners, Limited, and Noranda Copper and Brass, Limited.

In addition, a trip to the plants of the Aluminum Company of Canada, Limited, at Arvida in the Saguenay Valley, referred to in earlier issues of the JOURNAL, is planned starting Wednesday night and continuing through Thursday (Details of this trip are outlined on the following page).

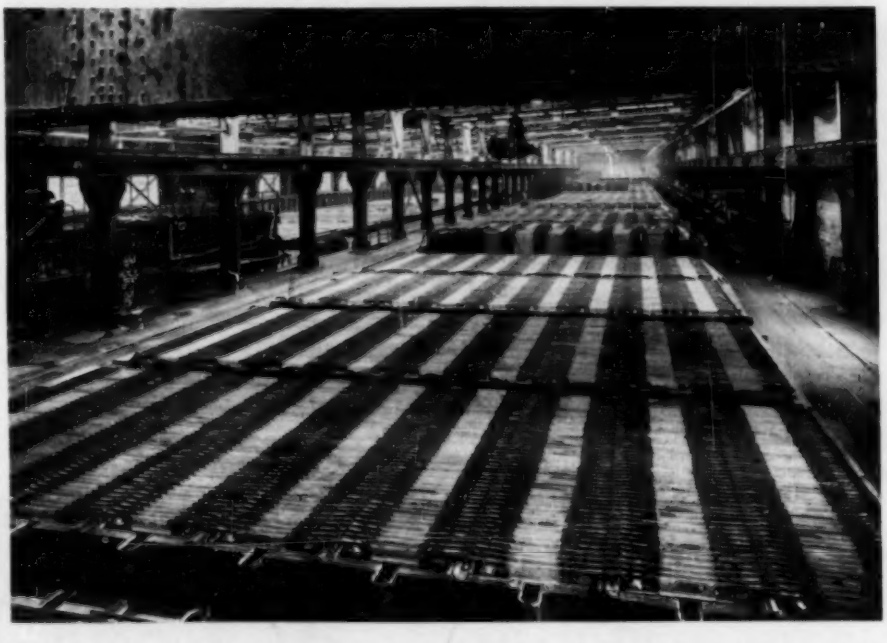
McGill University

The trip to McGill University includes a conducted tour through the Eaton Electronics Research Laboratory and to the cyclotron in the McGill Radiation Laboratory.

The Eaton Electronics Research Laboratory is one of the two research institutes that have been organized within the Department of Physics at McGill University. Its purpose is to train graduate students in the various branches of physics that are included in the terms Radio Physics and Electronics.

The work of the laboratory tends toward pure research, rather than application or development, but most of the pure research is related to applied fields of electronics. As examples, the research in the field of solid state is related to modern developments in the use of semiconductors in electronics, and the work on the optics of radio systems is associated with the development of radio antennae. Other work is on high frequency tubes, the investigation of the primary and secondary emission of electrons, and various problems in physical electronics. Fundamental circuit problems is another field of interest pursued at the laboratory.

The Radiation Laboratory consists mainly of a cyclotron with its auxiliary equipment, and the main work is basic research in nuclear physics. The cyclotron is characterized by a maximum energy represented by 100,000,000 volts. The major item of work carried on concerns the discovery of new isotopes and about 25 of these have been discovered over the last three years. Some spectroscopic work is carried on, both optical and microwave.



Canadian Copper Refineries, Limited—General view of a portion of the electrolytic tank house

Canadian Copper Refiners, Ltd.

The plant of Canadian Copper Refiners, located in Montreal East, offers a tour through a modern electrolytic refinery.

The heart of the process is the tank house with a rated capacity of 11,000 tons of cathodes per month. Servicing the tank house is the casting department, where anodes are cast for refining, and where refined copper cathodes are melted into marketable shapes. Melting is done in oil-fire reverberatory and electric arc furnaces.

In the silver refinery, silver and gold are recovered from the electrolytic anode slimes. Selenium and tellurium are also recovered, Canadian Copper Refiners Limited being the largest selenium producer in the world. Various marketable grades of copper sulphate are produced from tank house electrolytes and silver refinery liquors.

Noranda Copper and Brass, Ltd.

Adjoining the copper refinery is the plant of Noranda Copper and Brass Limited, where copper and copper alloys are produced in the form of strip, rod, wire, and tubing. These are the basic raw materials which are converted by fabricators into manufactured goods. Noranda Copper also produces finished products, such as welding rod, copper-

Aerial view closeup of the all-aluminum Arvida bridge and Shipshaw No. 2 plant

covered ground rod, brass and copper pipe, water tubing, duplex tubing, and heat-exchanger tubing.

Aluminum Company of Canada, Ltd.

Since interest in the extensive industrial development of the Saguenay Valley area is very general, members have been invited to visit the plants of the Aluminum Company of Canada, Limited, at Arvida, Quebec.

Arrangements will be made to leave Montreal on Wednesday evening, October 29, by rail, arriving in Arvida the following morning. During Thursday there will be conducted tours through the Shipshaw hydroelectric plant, the very modern Arvida Research Laboratory of Aluminium Laboratories Limited, and the Arvida Works of the Aluminum Company. Transportation back to Montreal will also be by rail, leaving Arvida Thursday evening and arriving in Montreal Friday morning. A reservation card for this trip will be enclosed with the Program Booklet. This should be filled out and returned to Montreal by October 15. Estimated cost of the trip, based on a lower berth and including breakfast and dinner at the Saguenay Inn, is about $35.

The Aluminum Company operates four smelters in the Province of Quebec, the largest being at Arvida. Bulk of the power for aluminum reduction at Arvida is provided by the nearby 1,200,000 horsepower Shipshaw No. 2 powerhouse. The visitors will have ample opportunity to see both of these large installations. The Arvida smelter is the world's largest.

They will also see how the tremendous amount of power developed by the Saguenay system is used to make aluminum, and will be able to follow the various stages in the production of finished aluminum ingot from the basic raw material, bauxite, which is mined and shipped from British Guiana.

The whole complex installation covers an area about 1½ miles long and ¾ mile wide. The chief buildings of the plant are the reduction plant proper, consisting of 22 potlines, a carbon plant, alpaste plant, rod mill, two ore plants, eight miscellaneous plants, research laboratory, two maintenance shops, three steam plants, and the offices.

At the new Research Laboratory a small modern theatre is located in the building. Here a film will be shown giving the highlights of the entire industry in a complete and carefully prepared form. Also, there will be visits to one of the Bayer Alumina plants, the Carbon Electrode plant, one or more of the potlines in the aluminum plant, and to the company's Caustic Chlorine plant. The latter, containing the latest Mathieson type cells, should interest many.

The Aluminum Company will be host at a luncheon in the Saguenay Inn on the day of the visit to Arvida.

It is the intention to make this trip as complete and interesting as possible and no effort will be spared in achieving this end.

Technical Program

The technical program for the Montreal Meeting will include symposia on Batteries, Corrosion, Electric Insulation, Electrodeposition, and Industrial Electrolytics. The number and quality of the papers to be presented promise particularly interesting sessions. Also planned is a joint Battery–Electric Insulation round table discussion. The complete technical program will appear in the October issue of the JOURNAL.

Luncheons

On Monday, October 27, will be held the general Society luncheon, to which

Shipshaw No. 2—Interior view showing aluminum railings

the ladies are invited. A prominent speaker, who will be announced later, will be present to welcome members and guests to Montreal. Dr. William Blum will be honored at the luncheon as the recipient of an Honorary Membership in the Society. Mr. George Hogaboom will speak regarding Dr. Blum's contributions to science.

Plans for the Division luncheons will be announced later.

Dinners and Entertainment

An informal dinner, preceded by a general get-together and cocktails, will be held on Monday evening. Special entertainment will follow.

The Acheson Medal Banquet will be held on Tuesday evening, October 28, at which the Acheson Medal and Prize will be presented to Dr. John Wesley Marden. The banquet will be preceded by a reception for him. Dr. Charles Slack, Manager of Atomic Power Division of Westinghouse Electric Corporation, will speak on both the personal and scientific accomplishments of the Medalist, and Dr. Marden will deliver an address.

Ladies' Events

The Ladies' Committee, headed by Mrs. C. Bruce Brown, has developed a program designed to provide interesting entertainment for the ladies during their stay in Montreal. Starting these activities will be a get-acquainted tea on Sunday afternoon, given by the Ladies' Committee. On Monday afternoon, a visit to one or more of the local points of interest has been arranged. On Tuesday morning, a trip is planned to outlying areas in the Laurentian Mountains. Luncheon will be served en route at one of the many well-appointed hotels. The return will be timed conveniently early for attendance at the Acheson Medal Dinner.

For Wednesday afternoon the ladies will be offered a number of alternate short trips around the city.

There will be an information desk near the general registration desk for the benefit of visiting lady guests.

Hotel Reservations

The Sheraton-Mount Royal Hotel, Convention Headquarters, is located at Peel Street, between Sherbrooke and St. Catherine Streets, Montreal. It is recommended that requests for reservations be made early and these should be sent direct to Reservation Manager, Sheraton-Mount Royal Hotel, Montreal, Canada. In the case of members, it is preferable to use the reservation card which will be received with the Program Booklet.

National Instrument Conference and Exhibit

The forthcoming Seventh National Instrument Conference and Exhibit, to be held in the Public Auditorium, Cleveland, Ohio, September 8–12, will include as speakers more than 100 outstanding scientists and technical specialists from government, educational, and industrial organizations.

This gathering, sponsored by the Instrument Society of America, will include the American Institute of Physics, the American Society of Mechanical Engineers, the American Institute of Electrical Engineers, the Institute of Radio Engineers, the Cleveland Physics Society, and the Scientific Apparatus Makers Association. An attendance of over 10,000 is expected.

Pennsalt and Sharples Chemicals Unite Research

The Research Department of Sharples Chemicals, Inc. will be integrated with the Research and Development Division of the parent company, the Pennsylvania Salt Manufacturing Company, according to an announcement by W. A. LaLande, Jr., manager of Pennsalt's division. The integration is to take place between June 15 and September 15.

Dr. LaLande states that the physical combination of the two experienced organic research groups at Whitemarsh Research Laboratories, with the subsequent daily interchange of ideas and know-how gives Pennsalt an unusually strong organization for attacking a wider range of problems in organic technology, and for developing new and improved products

ASTM Celebrates 50th Anniversary

The American Society for Testing Materials, at its 50th Anniversary Meeting, held at the Hotels Statler and New Yorker in New York City during the week of June 22, emphasized the importance of standards and research in materials. An unusually strong technical program included 165 papers in some 40 formal and informal technical sessions, and 70 reports from the technical committees. Added to this were 450 technical committee meetings and the society's largest exhibit of testing apparatus and scientific instruments. The meeting attracted a record number of engineers and materials men, totalling 2606.

Among the features of the meeting were the 1952 Awards of Merit, given to ten technical leaders in the field of engineering materials; the Marburg Lecture by Dr. R. C. McMaster, Battelle Memorial Institute, on "Non-Destructive Testing"; and the Gillett Lecture by Norman L. Mochel, Westinghouse Electric Corporation, on "Man, Metals and Power."

ALCOA Installs Huge Rolling Mill

A huge new rolling mill, costing about $4,500,000 and capable of producing extra-wide, tapered sheet and plate for aircraft, will be installed at Aluminum Company of America's Davenport, Iowa, works by late 1953.

Equipment for the mill—which will be one of the largest and most modern in the aluminum industry—will be designed, installed, and operated by ALCOA under terms of a lease arrangement with the United States Air Force's Air Materiel Command. The Air Force, in turn, will have first call on production of the new mill.

Dr. Blum to Be Honored at Montreal

Dr. William Blum, former Chief of the Electrodeposition Section of the National Bureau of Standards, and Past President of The Electrochemical Society, was elected to Honorary Membership in the Society at a meeting of the Board of Directors on June 27. The presentation to Dr. Blum will be made during the Montreal Meeting, at the Society luncheon on Monday, October 27, with Mr. George B. Hogaboom making the presentation speech (An account of this will be published in the JOURNAL following the meeting).

MEETINGS OF OTHER ORGANIZATIONS

SEVENTH NATIONAL INSTRUMENT CONFERENCE, Cleveland, Ohio, September 8–12.

SEVENTH NATIONAL CHEMICAL EXPOSITION, Chicago Coliseum, Chicago, Ill., September 9–13.

AMERICAN CHEMICAL SOCIETY, national meeting, Atlantic City, N. J., September 14–19.

NATIONAL METALS SHOW, Philadelphia Auditorium, Philadelphia, Pa., October 20–24.

TENTH ANNUAL PITTSBURGH DIFFRACTION CONFERENCE, Mellon Institute of Industrial Research, Pittsburgh, Pa., November 6–7.

SECTION NEWS

Cleveland Section

At a meeting of the Cleveland Section of The Electrochemical Society held on May 16, the results of the mail ballot for the election of officers for the 1952-53 season were announced. The names of the elected officers are as follows:

Chairman—L. E. Pucher
Vice-Chairman—N. C. Cahoon
Treasurer—W. H. Stoll
Secretary—J. M. Margolis

N. C. Cahoon, *Secretary* (1951–52)

Detroit Section

The new officers for the Detroit Section who will serve during 1952–53, elected at the closing spring meeting, are as follows:

Chairman—Glenn Coley
First Vice-Chairman—Dan Trivich
2nd Vice-Chairman—Wright Wilson
Secretary-Treasurer—Gerald V. Kingsley
Member of Advisory Committee—Henry Brown

C. O. Durbin, *Chairman* (1951–52)

India Section

At the Second Annual Meeting of the India Section, which took place on June 27 at the Indian Institute of Science, Bangalore, the officers listed below were elected for the 1952–53 season:

Chairman—M. S. Thacker
Vice-Chairman—Charat Ram
2nd Vice-Chairman—K. Rajagopal
Secretary-Treasurer—J. Balachandra

J. Balachandra, *Secretary-Treasurer*

DIVISION NEWS

Battery Division

The report of the Nominating Committee of the Battery Division has been submitted by the Chairman, offering the following nominations to be voted on at the Montreal Meeting:

Chairman—Eugene Willihnganz
Vice-Chairman—N. C. Cahoon
Secretary-Treasurer—E. J. Ritchie
Executive Committee—Arthur F. Daniel and Upton B. Thomas

According to the bylaws of the Division, names of the nominees are to appear in the Journal prior to the meeting at which they will be voted upon. Other nominations may be made either by mail or from the floor. Such nominations should carry with them an assurance of the willingness of the nominee to serve.

J. N. Mrgudich, *Chairman* (1951–52)

PERSONALS

Carl W. Borgman has been named President of The University of Vermont and State Agricultural College, Burlington, Vt. Dr. Borgmann was previously at the University of Nebraska, Lincoln, Neb.

Robert M. Parke, formerly of Battelle Memorial Institute, Columbus, Ohio, is now at the General Electric Research Laboratory, Schenectady, N. Y.

David Aitken has left the Cleveland Electric Illuminating Company, Cleveland, Ohio, to join the Brodhead-Garrett Company of Cleveland.

William B. Roberts, formerly of Sarkes Tarzian, Inc., Bloomington, Ind., has joined P. R. Mallory & Co., Inc., Rectifier Division, Indianapolis, Ind.

M. Merlub-Sobel, Associate Professor of Chemical Engineering, Hebrew Institute of Technology, Haifa, Israel, is on a Sabbatical leave from the Institute and plans to remain in the United States for one year. He is now at 265 Jackson Avenue, Jersey City, N. J.

K. L. Ramaswamy, formerly deputy superintendent (Production), is now Technical Secretary to Managing Director, in the Sindri Fertilizers & Chemicals Ltd., Sindri, India.

M. S. Thacker, Indian Institute of Science, Bangalore, attended the Conference Internationale des Grands Reseaux Electriques held in Paris during May–June, as Chairman of the Conference. He also visited some laboratories in Paris and London during this tour.

Wilbur H. Rose has transferred to Olin Industries, Inc., Covington, Tenn., from the company's plant in New Haven, Conn.

Correction

Paul L. Howard is now associated with the Yardney Electric Corporation. In the August Journal the company name was incorrectly given as the Yardley Corporation.

NEW MEMBERS

In July 1952 the following were elected to membership in The Electrochemical Society:

Active Members

Albert J. Cornish, Westinghouse Research Laboratories, East Pittsburgh, Pa. (Electronics)

Tadayoshi Fujiwara, c/o I.C.I. (Japan) Ltd., 435 Tokyo Hotel Building, Tokyo, Japan (Corrosion, Electrodeposition, Electronics, and Theoretical Electrochemistry)

Victor C. Garbarini, E. I. duPont deNemours & Co., Experimental Station, Wilmington, Del. (Electronics)

Harnam S. Gujral, Technical Development Establishment (I.E.) Sunderwala Camp, Dehradum (U. P.) India (Battery)

Floyd Mickelson, Motorola Inc., Plating Dept., 1327 W. Washington Blvd., Chicago, Ill. (Corrosion, Electrodeposition, Electronics, and Theoretical Electrochemistry)

James H. Moore, National Research Corp., mailing add: 27 Fuller Ave., Swampscott, Mass. (Electronics and Electrothermic)

Kelso B. Morris, Department of Chemistry, Howard University, Washington, D. C. (Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

John A. Ricketts, Western Reserve University, mailing add: 1650 Wyandott Ave., Lakewood 7, Ohio (Theoretical Electrochemistry)

Elmer M. Schneider, Westinghouse Electric Corp., mailing add: Apt. 8B, Unit 3, Victory Hts. Apts.,

New Dues for 1953

In accordance with the action of the Board of Directors at the May 4th meeting to increase the dues 25 per cent, the new rates, effective January 1, 1953, will be:

Active members	$15.00
Associate members	9.50
Student members	3.00

The action to raise the Society dues was deemed necessary in order to meet the continued rise in the cost of printing, paper, and general expenses.

Grand Central Ave., Horseheads, N. Y. (Electronics)

Otis J. Streever, Newport News Shipbuilding and Dry Dock Co., Newport News, Va. (Corrosion and Theoretical Electrochemistry)

Joseph E. Weber, Chemistry Department, Bowling Green State University, Bowling Green, Ohio (Electro-Organic)

Associate Members

Anthony J. Certa, Philco Corp., Lansdale, Pa. (Electronics)

Morris Eisenberg, University of California, mailing add: 1508 Oscar St., Richmond, Calif. (Electrodeposition and Theoretical Electrochemistry)

Sudarshan D. Gokhale, India Government Mint, mailing add: 176A, Parshuramwadi, Girgaum, Bombay 4, India (Electrodeposition, Electrothermic, Industrial Electrolytic, and Theoretical Electrochemistry) (Formerly Student Associate Member)

Eugene B. Shultz, Jr. Illinois Institute of Technology, mailing add: 2847 W. Giddings, Chicago, Ill. (Corrosion and Theoretical Electrochemistry)

LETTER TO THE EDITOR

Metallic Water

Dear Sir:

Enclosed herewith please find literature pertaining to "metallic water" invented by the writer, and he entreats you to kindly arrange for publication of it in the American academic circle through your esteemed bulletin.

It is the writer's only aim to be enlightened by any criticism or comments on a few problems contained in the statement, the researches which are left incomplete at this time.

It would be very gratifying to him if he could see himself in print and be favored with useful reflections upon the proposition.

General explanation.—This invention relates to electrolysis of metals, such as iron, tin, copper, lead, gold, silver, platinum, zinc, aluminum, magnesium, manganese, bismuth, cadmium, etc.

Through process of this invention, we can obtain various stable ionized metallic solutions by means of a single medium of water, instead of media of chemicals as has hitherto been practiced. We can thereby obtain useful chemicals and medicines.

So far, it has been next to impossible to obtain a solution of metal of single componency by the medium of water itself, while it is widely known that some liquidized metals can be obtained through the process of electrolysis by ionizing in solution of salts or dissolving in a solvent of specific chemical compounds.

Process.—A partition cylinder (2) is placed in a cell (1), the cylinder having a branch tube (3) with its end downward, as shown in Fig. 1. The bottom of the cylinder is covered with a piece of porous tissue (4).

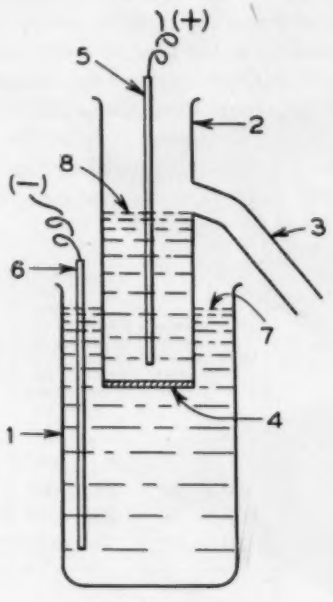


Fig. 1

Place inside the cylinder a metal piece (5) to be electrolyzed and put another piece of metal (6), such as platinum stick, outside the cylinder but inside the cell. Pour water into both the cell and the cylinder up to the level marked (7). The former (5) will be connected with the positive pole, and the latter (6) with the negative. Then charge with direct current of adequate voltage, when electrolytic action will start.

After a certain amount of time, the metal (5) will be dissolved or ionized, escaping through the porous tissue (4) toward the negative pole. At the same time, a part of the ions, passing into hydroxide, will deposit over the porous tissue, which will thereby form a semi-permeable membrane, and it will cause the augmentation of electric resistance.

When the resistance increases to a certain point, the traveling of the greater portion of dissolved metallic ions toward the negative pole will be checked by the deposit, while only the water outside the cylinder or in the negative

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pole chamber will be percolated through the tissue into the positive chamber.

Thus the water in the cylinder will rise to the level (8) where the branch tube emerges. The overflow of the aqueous solution of metal ions will then run through the branch tube outward, drop by drop. The dissolved substance thus obtained is chemically neutral, despite the fact that it has been obtained from the positive pole chamber. Though it contains a negligible minor quantity of hydroxide, it maintains the ionized condition permanently.

Experiments.—The time required for the overflow of metallic water varies according to the kind of metal and the direct current voltage; the economical voltage ranges from 100 to 200 volts.

Usually it requires only a little over 10 hours for iron, zinc, and copper, while in the case of gold or platinum, scores of hours are required.

Metal dissolved	Volts	Hours before solution level rises	Hours before solution overflows	Volume of solution obtained for 30 hr	Ingredient
				cc	%
Zinc	100	20	20	500	0.003
Iron	100	20	30	400	0.010
Copper	100	30	30	450	0.0036

Of the various metallic waters obtained through the above mentioned process, zinc, copper, and iron waters may keep within a very small quantity of contamination of hydroxide for the first 3 months, but their principal action for either medical, insecticidal, or sterilizing purposes is little affected.

Utility.—Zinc, iron, and bismuth waters are now being applied to medical treatment in some clinics and hospitals. The first mentioned is being used as eye lotion and remedies for skin diseases and inflammation of the mucous membrane. It is also used as effective styptic. The second is a tonic for anemia. The third one is an effective binding medicine. From their experiments by several physicians as well as the inventor, these three products revealed marvelous effects on the ailments.

From the viewpoint of gerontology, too, the intake of minerals to the human body has come to be much talked of nowadays.

The inventor believes that his metallic waters leave to the academic circles of physical chemistry many objects for researches. He dares hereby report to the academic circle of the U. S. on his invention and at the same time offers some questions as aforementioned, on which he desires enlightenment.

The swelling up of water in the cylinder from the level (7) up to (8) is an unexplainable phenomenon, which comes out in the course of the process of producing the metallic water invented by the writer (Japanese Patent No. 176,670, Feb. 27, 1948).

Some Japanese chemists simply attribute this phenomenon to an osmotic pressure. This conclusion may be justifiable from the viewpoint of thermodynamics only in the case where the density of liquid waters both within and outside the cylinder is taken into consideration as important factors.

Granting this conclusion to be convincible, it cannot have any connection with electric current. In other words, the swelled water surface shall be maintained on the level of (8) as ever, even after the contact is broken. Nevertheless, the water level comes down to the level of (7) as soon as the contact is broken, according to the writer's repeated experiments. This physical phenomenon or chemical action should bear a nomenclature of "Electro-osmotic Pressure."

I should think, however, it would be rather adequate to believe that this phenomenon is due to electrolytic solution pressure. Japanese academic circle of chemistry does not approve of it for the sole reason that the "Electrolytic solution pressure shall be constant."

One more thing to which the writer desires to draw public attention is the fact that the water in the cylinder is generally considered to be acidic; but, it is in fact found to be neutral.

* * *

After repeated experiments in a similar way to those of zinc, iron and copper, the inventor has at last succeeded in obtaining a new substance to be called "mercuric water." This new solution is transparent, quite the same as water in appearance, but weighty in its specific gravity.

The quantitative analysis revealed that it contains 0.017 grams of mercury per 100 cc of the mercuric water; *p*H 6.3.

This substance is of wide application, especially in clinic and pharmaceutics circles.

Kogoro Murakoshi
Tokyo University,
Tokyo, Japan

BOOK REVIEWS

RADIOLOGICAL MONITORING METHODS AND INSTRUMENTS, National Bureau of Standards Handbook 51. For sale by Superintendent of Documents, U. S. Government Printing Office Washington, D. C., 1952. 33 pages, price 15 cents.

This Handbook summarizes the problems involved in radiation monitoring and discusses very briefly the various types of measurements that it may be necessary to make to determine the hazard present and also the types of instruments used in making these measurements. No detailed discussions are given nor recommendations of any particular instruments. It is a concise report on the subject which should constitute an excellent guide for all who work with radioactive materials or other sources of radiation, such as x-ray equipment.

J D. STRUTHERS

INTERNATIONAL COMMITTEE OF ELECTROCHEMICAL THERMODYNAMICS AND KINETICS: Proceedings of the Second Meeting, 1950. Published by Libreria Editrice Politecnica Cesare Tamburini, Milan, 1951. xvi + 407 pages, 3800 lire.

This attractive volume contains the papers and discussion presented to the International Committee of Electrochemical Thermodynamics and Kinetics at its second meeting held in Milan, September 18–22 1950. Two brief introductory sections and an appendix also give an account of the business transactions of the Committee. The authors of papers represented the following nations: Belgium, Canada, France, Germany, Great Britain, Italy, Spain, and the United States. Representatives from The Netherlands, Norway, and Switzerland were also in attendance. The bulk of the papers are printed in French, an occasional paper in English or German.

The papers are grouped under the following headings: Electrochemical Equilibrium, Electrochemical Kinetics, Corrosion, Applications to General and Analytical Chemistry, Polarography, Nomenclature, and Fundamental Definitions.

It is difficult to give a comprehensive review of the entire volume. Among the papers which interested this reviewer may be mentioned: the work of Delahay, Pourbaix, and Van Rysselberghe on the potential-*p*H equilibria for lead,

silver, zinc, and their salts, and for oxygen, peroxide, and water; Valensi's work on the potential-*p*H equilibria for sulfur and its compounds; Piontelli's remarks on electrochemical kinetics; Piontelli and Poli's work on metal polarization; Pourbaix and Van Rysselberghe's work on corrosion and passivity; Charlot and Gauguin's applications to analytical chemistry; Erich Lange's masterful "Ueber elektrochemische Grundbegriffe." These papers are extremely stimulating to the worker in electrochemistry, both because of the beauty of the experimental results, and because of the logical clarity of the theoretical formulations. An American reader would have to familiarize himself with the European formulation of chemical thermodynamics, in terms of affinities rather than free energy changes.

The volume is attractively printed and seems to be reasonably free from misprints and errors. The figures are clearly reproduced and easily legible. In conclusion, it might be well to quote one of the resolutions adopted at this meeting (p. 393): "The International Committee of Electrochemical Thermodynamics and Kinetics most strongly recommends to all electrochemists, physical chemists, physicists, and engineers the exclusive use of *standard electrode potentials* based on the so-called "European" convention (so-called "reduction potentials"), i.e., *potentials* which express the potential of *the metal with respect to the solution*, except for an indeterminate additive constant. "Noble" potentials are therefore positive, and the positive terminal of a battery is that terminal whose potential has the higher positive value."

ANDRÉ J. DEBÉTHUNE

PAINT AND VARNISH PRODUCTION MANUAL by V. C. Bidlack and E. W. Fasig. Published by John Wiley & Sons, Inc., New York, 1951. vii plus 288 pages, $6.50.

The publication of this book was sponsored by the Federation of Paint and Varnish Production Clubs. It provides a compact picture of the modern paint and varnish plant, and covers all phases of the manufacturing operation. The book is divided into ten chapters which deal with such topics as Plant Location, Plant Design, Choice of Equipment, Raw Material Handling, Production Scheduling, Personnel, and Safe Operation.

Each topic is discussed in a thorough but concise manner which makes the book of particular interest to those in supervisory capacities. The book does not provide detailed information on the formulation or development of organic coatings.

Chapter One titled Physical Facilities provides specific recommendations regarding plant location, material handling, and power requirements. A suggested layout for a modern paint factory embodying the latest developments in design and equipment and similar suggested layout for a varnish plant are presented in subsequent chapters. The section entitled Manufacturing Operations presents a wealth of information concerning good practice in the operation of a paint factory. The chapters on personnel and cost accounting recommend modern business practices applicable to this industry, while the discussion on research and development recommends an organizational plan for laboratory work and provides a section on methods of test with an excellent bibliography covering development methods. The final chapter on fire-protection safety and health lists the common hazards encountered in the manufacture of organic coatings and suggests protective measures. The book provides a valuable source of information for those concerned with the manufacture of organic coatings. While each topic is discussed somewhat briefly a very complete bibliography is included which greatly enlarges the scope of the book.

J. C. OSTEN

LITERATURE FROM INDUSTRY

ELECTROMAGNETIC PUMP. A new a-c electromagnetic pump with no moving parts, for pumping liquid metals and other low-resistance conducting fluids at temperatures up to 1000° F is described in special folder. General Electric Co. P-55

AUTOTRATOR. Illustrated folder explains simple and accurate operation of the Coleman Autotrator for automatic titrations. Economical and "made for the modern laboratory." Burrell Corp. P-56

INSTRUMENTS AND RADIOCHEMICALS. New 2-color condensed catalogue listing latest instruments and radiochemicals for radioisotope applications in the medical, educational, industrial, and research fields is available on request. Nuclear Instrument & Chemical Corp. P-57

INDUSTRIAL DETERGENT. New service bulletin entitled "How to Make Industrial Work Come Clean," explains how Pensal W works to remove heavy soils and grease—and gives directions for the use of this heavy-duty detergent on clothes, oily wipers, etc. Pennsylvania Salt Mfg. Co. P-58

ALKALINE TIN-LEAD STRIPPER. Literature available about a new alkaline chemical for rapid dissolving of tin, lead, and tin-lead alloys. Due to alkaline nature, there is no attack upon base metals such as copper, brass, bronze, steel, and stainless steels. Does not deteriorate with age. Enthone, Inc. P-59

SUBMERGED ELECTRODE SALT BATHS. New booklet describes seventeen ways in which the submerged electrode salt bath furnace increases metal heat-treating efficiency on 10 specific heat-treating applications in a range from 1100°F to 2400°F. Ajax Electric Company Inc. P-60

WATER DEMINERALIZER. Bulletin describing the Barnstead Bantam water demineralizer for laboratories. Seven important features listed including new direct-reading type meter and simple, efficient operation. Eberbach & Son Co. P-61

MECHANICAL PROPERTIES OF NICKEL DEPOSITS. Booklet containing 12 pages, 13 charts, 3 tables, and numerous photomicrographs shows the wide range of properties that may be obtained in electrodeposited nickel by varying the solution and plating procedure. Data on the interrelation of ductility, strength, and hardness in deposits that may be obtained in present-day rapid nickel-plating solutions. International Nickel Co., Inc. P-62

LABORATORY EQUIPMENT. July bulletin "Lab Oratory" features new items of laboratory equipment including large selection of superior clamps, scales, containers, cabinets, etc. Schaar and Co. P-63

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

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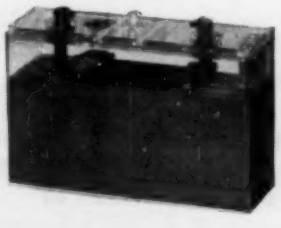

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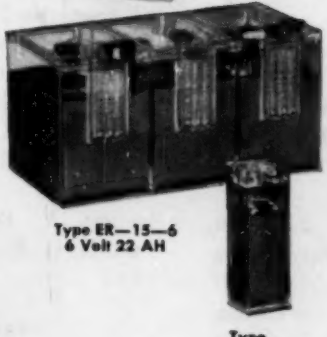

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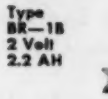
10 Volt 8 AH



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RECENT PATENTS

Selected for electrochemists by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

May 6, 1952

Cotton, W. J., 2,595,227, Electrical Oxidation of Aralkyl Hydrocarbon

Kalling, B. M. S., Sundgren-Walldén, R. S. M., Walldén, S. J., and Sivander, K. A., 2,595,387, Method of Electrolytically Recovering Nickel

Lewis, R. W., and Richardson, R. P., 2,595,963, Primary Electric Cell

May 13, 1952

Stuffer, R. S., 2,596,307, Process of Electrostripping Electrodeposited Metals

Cooper, D. P. Jr., 2,596,469, Tantalum Carbide Filament Electric Lamp Containing Hydrogen-Volatile Hydrocarbon Mixture

Ranby, P. W., 2,596,509, Titanium Activated Barium Pyrophosphate Phosphor

Watkins, G. B., and Gaiser, R. A., 2,596,515, Coating Vitreous Substances

Meiklejohn, G. T., 2,596,583, Electrolytic Cell

Martin, D. L., 2,596,705, Magnetic Alloy

May 20, 1952

Marsal, P. A., and Fox, R. P., 2,597,116, Air Depolarized Cell

Schumacher, E. A., and Brooks, P. S., 2,597,117, Aqueous Electrolyte for Primary Galvanic Cell

Brooks, P. S., and Schumacher, E. A., 2,597,118, Support for Primary Galvanic Cell Electrolyte

Schumacher, E. A., and Bennett, R. J., 2,597,119, Electrode for Air Depolarized Primary Galvanic Cells

Tama, M., Tama, M., and Hoff, J. L., 2,597,269, Apparatus for the Mold Casting of Metals

Cook, W. J., and Tuck, J. H., 2,597,296, Forming Starting Sheets for Electrolytic Refining of Nickel

Dale, H., 2,597,302, Process for Utilization of the Gas Washing Lye from Aluminum Electrolysis in Cryolite Production

Coleman, J. J., and Louzos, D. V., 2,597,451, Primary Cell; 2,597,452, Primary Cell; 2,597,453, Primary Cell; 2,597,454, Primary Cell, 2,597,455, Primary Cell; 2,597,456, Primary Cell.

Jackson, J. H., and Simmons, O. W., 2,597,495, Hot Workable Nickel Alloy

Taylor, M. C., 2,597,545, Electrolytic Method

Froelich, H. C., 2,597,631, Method of Preparing Barium Silicate Phosphor

McKeag, A. H., and Ranby, P. W., 2,597,660, Zinc Sulfide Type Phosphors

Nicholls, M. B., 2,597,665, Thermocouple

Salisbury, W. W., 2,597,752, Thermoelectric Power Generator

May 27, 1952

Eichner, F. L., 2,598,043, Process of Preparing Planographic Printing Plates

Coleman, J. J., 2,598,226, Dry Cell and Separator Therefor

Cox, R. B., 2,598,228, Electrolytic Apparatus

Teal, G. K., 2,598,317, Preparation of Two-Sided Mosaic Screens

Teal, G. K., 2,598,318, Method of Thickening Relatively Thin Apertured Metallic Screens

Andrews, J. W., 2,598,486, Electrolytic Tin Plating Baths

June 3, 1952

Handwerk, E. C., and Mahler, G. T., 2,598,741, Smelting of Zinciferous Ore

Handwerk, E. C., and Mahler, G. T., 2,598,742, Smelting of Zinciferous Ore

Waring, R. K., Fetterolf, L. D., and Hurst, T. L., 2,598,743, Zinc Smelting

Handwerk, E. C., and Mahler, G. T., 2,598,744, Smelting of Zinciferous Ore

Handwerk, E. C., and Fetterolf, L. D., 2,598,745, Smelting of Zinciferous Ore

Frary, F. C., 2,598,777, Recovering Gallium from Metallic Aluminum

Renman, G., 2,598,833, Process for Electrolytic Deposition of Iron in the Form of Powder

Holt, M. L., and Seim, H. J., 2,599,178, Electrodeposition of Alloys of Molybdenum with Cobalt, Nickel, and Iron

Hopkins, R. K., 2,599,179, Furnace Electrode

Bennett, A., Prince, D. H., and Edwards, G. E., 2,599,363, Electrolytic Cell

June 10, 1952

Tuwiner, S. B., and Korman, S., Application 30,750, Dialytic Purification of Used Copper-Refining Electrolyte

Justin, F. H., Application 48,672, Galvanic Anode Assembly

Shwartzman, G., 2,599,587, Process of Preparing an Antibacterial Substance from Pyridoxamine

Lark-Horovitz, K., and Siegel, S., Application 64,034, Method of Altering the Electrical Characteristics of Semiconductors

Rajtora, V., 2,599,779, Electric Furnace

Ellsworth, J. T., Ellsworth, M., administratrix of said Ellsworth, J. T., deceased, 2,599,816, Purification of Zinc Electrolytes

Hackmann, J. T., 2,600,054, Process for Preparing Esters

Gelfand, M., and Richman, I. M., 2,600,107, Electrolytic Bone Decalcification Process

Sagen, G., 2,600,171, Regeneration of Chromic Acid Baths Utilized in Electrodeposition of Chromium

Caird, D. W., 2,600,202, Method for Polymerizing Chlorotrifluoroethylene

Prener, J. S., 2,600,263, Arsenic Activated Zinc Sulfide Phosphor and Method for Making Same

Tuttle, C. M., 2,600,343, Method of Making Conductive Patterns

Wernlund, C. J., 2,600,352, Bright Zinc Electroplating

June 17, 1952

De Voe, C. F., 2,600,490, Glass Melting Method

Ruedy, J. E., and Williams, F. E., 2,600,579, Method of Making Phosphor Screens

EMPLOYMENT SITUATIONS

Please address replies to box shown, c/o The Electrochemical Society, Inc., 235 W. 102nd St., New York 25, N. Y.

Positions Wanted

CHEMICAL ENGINEER, B.S. 1939, M.S. 1952, 6 years' industrial plus 4 years' Civil Service experience in electrochemical field (plating, batteries), supervision, development, research. Adaptable, mechanically inclined. Available September. *Reply to Box 349.*

ELECTROCHEMIST, Ph.D., industrial experience in deposition, corrosion, analytical instrumentation. Present salary $6500. Desires position in industry. Available in 15–30 days. *Reply to Box 350.*

Position Available

SUPERVISOR, Plating and Painting Departments of small manufacturing company in Philadelphia area. Must be qualified and experienced in production techniques and control methods. *Reply to Box A-241.*

Editorial

Electrochemists Contribute to Corrosion Progress

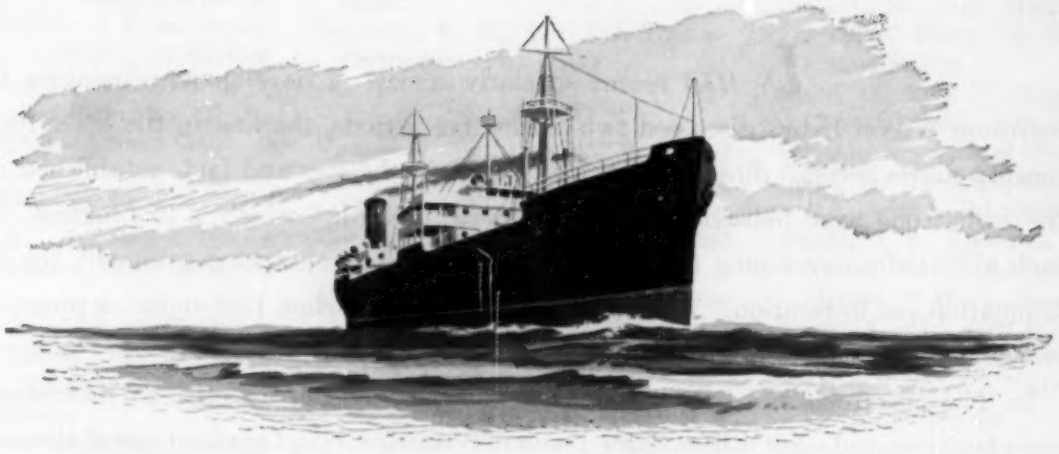
IN HIS recent scholarly review of developments relating to corrosion Wilson Lyons discussed two productive periods, the first in the early 19th century and a second, during which many of the "theories and facts established in the earlier one were rediscovered or elaborated, or both," which is in progress. In such a "rapidly developing field . . . it is well to look backward occasionally for illumination and inspiration." This "illumination" seems to show that enduring progress is being made in our Society.

In The Electrochemical Society, which has one division devoted to theoretical considerations and eight others slanted toward certain practical applications of electrochemical science in specific fields, corrosion phenomena have, through the years, received serious study and discussion. Our active (and prosperous!) Corrosion Division has among its members many of the foremost workers in this field. Typical of their activities is the "Corrosion Handbook," sponsored by the division, edited by our own Herbert Uhlig, and contributed to by many division members. The value of this work is confirmed by its financial success, the returns from which are being used to stimulate further electrochemical development, such as the Palladium Medal Award of the Society. The Handbook itself seems an enduring landmark and lighthouse for the guidance of wandering investigators.

At times when we may be wondering why we work to preserve and improve the Society—as thoughtful people often do about their activities—we can be assured that such accomplishments are real contributions to the peace, comfort, and rightness of human existance.

—R. J. McKAY

Electrochemistry at DOW



ELECTROCHEMISTRY goes to sea . . . to fight costly hull corrosion

Costly hull corrosion is now being controlled by an electrochemical method . . . cathodic protection.

This method has proved successful in combating corrosion in underground pipe lines, tanks and industrial equipment. Now it is being used, for the first time on a large American commercial vessel, by Dow on the "Marine Chemist," the 13,000 ton leased tanker which transports chemicals from Dow's Freeport, Texas plant to the east coast.

Hull corrosion results from small electric currents flowing through the sea from the more active to the less active parts of the hull, removing particles of metal from the active areas. This is prevented by transferring the current flow, and that's where cathodic protection comes in.

Magnesium anodes are installed on the sides of the ship's hull. Magnesium, a very active metal, becomes the most active area of the ship's hull, and current flows from it instead of the steel hull. Only the anodes, which can be inexpensively replaced, are corroded.

Dow's work in the development of cathodic protection is but one outstanding contribution of Dow, a producer of over 600 chemicals for industry and agriculture, in the field of electrochemistry.

THE DOW CHEMICAL COMPANY • MIDLAND, MICHIGAN

The magnesium anodes, shown here being installed on the "Marine Chemist," are about 20 inches in length and weigh 60 lbs. They were designed to last a year.

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Fiftieth Anniversary

HISTORY OF THE CORROSION DIVISION

*H. R. Copson**

The Corrosion Division of The Electrochemical Society was formed in 1942. Five other divisions were organized earlier and three later. Thus, while it was not among the first divisions, it is not a newcomer. In fact the Society's interest in corrosion stems back much earlier to the very beginnings of the Society. Papers on corrosion always have drawn a lively interest.

The first papers on corrosion appeared in 1903 in the third volume of the TRANSACTIONS, one dealing with galvanic corrosion and one with stray currents. Other papers soon followed and by the time of the first ten-year index there was an impressive array of articles, many of them dealing with "Electrolytic Corrosion." In essence, the lack of homogeneity in the metal was considered to be a major factor in corrosion, although the importance of oxygen and overvoltage were recognized. In 1905, the Society awarded $100 to A. T. Lincoln for his research on the electrolytic corrosion of brass. In 1908, President C. F. Burgess devoted his presidential address to "Corrosion of Iron from the Electrochemical Standpoint."

The first real symposium on corrosion took place in 1912 with six papers on "Corrosion of Iron and Steel." The effect of impurities on the corrosion behavior of iron continued to occupy considerable attention, until it was finally settled that some impurities, specifically copper, were beneficial in atmospheric corrosion. In 1922, R. J. McKay contributed his classic paper in the TRANSACTIONS establishing that concentration cells in the liquid environment could be a major cause of corrosion.

In 1921 a large symposium on corrosion was held, with Colin G. Fink presiding, at which 16 papers were presented. The Technical Committee on Corrosion was formed about this time. This committee can be considered the forerunner of the Corrosion Division. The officers of this committee as recorded in the TRANSACTIONS were as follows:

	Chairman		
1922–25	C. G. Fink	W. M. Corse	W. D. Richardson
1926–29	R. J. McKay	W. M. Corse	F. N. Speller
1930–33	F. N. Speller	R. J. McKay	U. R. Evans
1934	J. Johnston	U. R. Evans	F. J. Kenny
1935–39	S. M. Norwood	U. R. Evans	O. B. J. Fraser
1940–44	S. M. Norwood	F. N. Speller	O. B. J. Fraser
1945	S. M. Norwood	F. N. Speller	F. L. LaQue

Interest in corrosion continued to grow with a symposium in 1924 with B. D. Saklatwalla presiding, and another in 1930 with F. N. Speller presiding. The latter symposium dealt with the Prevention of Corrosion of Metals in the Automotive Industry. In 1933 the Technical Committee on Corrosion organized an International Convocation on Corrosion which was held in Chicago. Five of the eleven papers had foreign authors.

Beginning about 1930 the Corrosion Committee published reports summarizing progress in the field of corrosion during the year. These took the form of general reviews or of short abstracts. In 1935 these reports were formalized into detailed literature surveys. For a time U. R. Evans handled the eastern hemisphere, and S. M. Norwood or O. B. J. Fraser covered the United States. Subsequently the work was passed around with contributions by W. Z. Friend, W. D. Forging, J. F. Mason, and H. O. Teeple, and finally it was made a group undertaking.

The Society kept pace with the expanding interest in corrosion by presenting more frequent and larger symposia. Among these were: 1936, "Inhibitors," J. C. Warner presiding; 1938, "Corrosion and *p*H," R. M. Burns presiding; spring of 1939, "Corrosion of Alloys," T. P. Morral presiding; fall of 1939, "Influence of Cathodic Reactions on Corrosion," R. B. Mears presiding. In the spring of 1942, another large symposium involved 15 papers, with R. B. Mears presiding.

Other organizations were also taking an increasingly active part in the field of corrosion. In 1938 the American Coordinating Committee on Corrosion was organized, and in 1941 the first annual AAAS Gordon Research Conference on Corrosion was held at Gibson Island. About the same time the annual meetings of the Sea Horse Institute got under way at Kure Beach, North Carolina.

The Corrosion Division of The Electrochemical Society was organized on a formal basis in 1942. L. G. Vande Bogart was the moving spirit. Approval of the Board of Directors was obtained in May 1942, and a number of committees were formed which reported at the Detroit meeting in the fall of 1942. Bylaws were adopted and officers elected. Active participants in the organizational meeting were L. G. Vande Bogart, R. H. Brown, R. M. Burns, K. G. Compton, J. D. Hanawalt, F. L. LaQue, J. A. Lee, W. S. Loose, R. E. McNulty, R. B. Mears, J. C. Warner, W. A. Wesley, and others. The officers of the Corrosion Division have been as follows:

	Chairman	*Vice-Chairman*	*Secretary-Treasurer*
1942–44	L. G. Vande Bogart	H. H. Uhlig	R. H. Brown
1944–46	H. H. Uhlig	R. H. Brown	I. A. Denison
1946–47	H. A. Pray	H. J. McDonald	I. A. Denison
1947–48	H. J. McDonald	M. G. Fontana	I. A. Denison
1948–49	M. G. Fontana	I. A. Denison	J. M. Pearson
1949–50	I. A. Denison	J. M. Pearson	N. Hackerman
1950–51	N. Hackerman	H. R. Copson	J. M. Bialosky
1951–52	H. R. Copson	F. W. Fink	J. M. Bialosky

The Corrosion Division grew rapidly—from 80 members in 1943 to 250 in 1944. In a Directory of the Corrosion

*Research Laboratory, International Nickel Company, Inc., Bayonne, New Jersey.

Division, published in 1948, some 574 members were listed, although possibly some cancellations or deaths were included in this figure. The recently published Directory of Members of The Electrochemical Society lists 508 confirmed members of the Corrosion Division which makes Corrosion one of the larger divisions of the Society.

Every year since its organization the Division has sponsored a symposium on corrosion with the division chairman presiding. The only exception was in 1945 when the scheduled meeting was canceled because of the war. The Corrosion Division meetings are now held at the fall convention of the Society, although through 1948 they were held in the spring. The emphasis at these symposia has always been on fundamental considerations and the theoretical basis of corrosion.

In 1945 the National Association of Corrosion Engineers completed its organization and the first issue of the magazine, *Corrosion*, appeared in March 1945. While this organization embraces the entire field of corrosion it has emphasized the practical aspects. This division of interest undoubtedly will continue with many practical papers appearing in *Corrosion* and the more theoretical papers in the JOURNAL of The Electrochemical Society. The Corrosion Division provides a place for the discussion and publication of fundamental work which is necessary for future developments in the field of corrosion.

In 1947 The Electrochemical Society and the National Association of Corrosion Engineers organized a joint symposium on cathodic protection which was held in Pittsburgh. The papers presented were published in book form and have brought some profits to the Society. Other joint sessions have been held by the local sections of the two organizations. The Electrochemical Society was also one of the sponsors of the Pittsburgh International Conference on Surface Reactions which was concerned with corrosion.

After its organization, the Corrosion Division took over the activities of the Technical Committee on Corrosion. The annual literature surveys were continued through 1945. While these were useful there was a feeling they were not adequate because they always appeared a year later. A greatly expanded abstract service now appears monthly in *Corrosion*. More recently *Industrial and Engineering Chemistry* has been publishing an annual review of the new literature on Materials of Construction.

A major undertaking of the Corrosion Division was the "Corrosion Handbook." This was conceived at the time of the organization of the Division. The Board of Directors authorized the Handbook in 1943, and by 1944 all the chapters had been assigned on a voluntary basis. Most of the authors were active members of the Corrosion Division. Included was a Glossary of Terms Used in Corrosion which was published in the TRANSACTIONS as soon as complete. The contract for the "Corrosion Handbook" was placed with J. Wiley & Sons, Inc. in 1947 and the first copies appeared early in 1948.

The "Corrosion Handbook" is the most authoritative publication in the field of corrosion, and its success has been outstanding. Over 10,000 copies have been sold to date, and royalties have accumulated to over $16,000. This fund has been set aside to be expended by the Corrosion Division with the approval of the Board of Directors on projects relating to the corrosion program of the Society. The Corrosion Handbook Fund is administered by a committee consisting of the Chairman of the Corrosion Division, the Editor of the Handbook, a member of the Editorial Advisory Board of the Handbook, and a representative of the Board of Directors of the Society.

The fund has been used to establish a Prize Essay Contest for students in an endeavor to awaken interest in electrochemistry and corrosion. The subject of the present contest is, "The Electrochemical Nature of Corrosion." The fund has been used to defray part of the local expenses of foreign visitors to meetings of the Theoretical Division in Washington, Philadelphia, and New York. The fund also provides a reserve for expenses involved in a revision of the "Corrosion Handbook", which will be needed in due course.

In 1950 the fund was used to found the Palladium Medal of The Electrochemical Society. The Palladium Medal was established to encourage research and achievement in the study of corrosion of metals and its control. It is awarded in recognition of accomplishments in this field or in theoretical electrochemistry upon which our understanding of corrosion is based. The first award was made to Dr. Carl Wagner in the fall of 1951, who then delivered the first Palladium Medal Address.

The Corrosion Division is proud of its accomplishments, and is alive to the present trends. It is expected that important developments in corrosion will continue to be presented at its meetings. A list of authors of past papers would include practically all the great leaders in the field; many of these names have appeared in this history.

DEVELOPMENTS IN CORROSION DURING THE PAST FIFTY YEARS, A BRIEF REVIEW

*Herbert H. Uhlig**

One year after the founder members of the Society deliberated at their first meeting in Philadelphia, Willis R. Whitney, later to become 9th president of the Society, published his famous paper on the electrochemical theory of corrosion. The paper was widely read both here and abroad, and the ideas expressed were duly acclaimed or opposed, in either instance with great vigor. It was natural that the new Society, which occupied within its sphere of interest all matters electrochemical, should have immediately included corrosion as one of the subjects eligible for the lively and sometimes humorous discussions recorded at the early meetings.

In 1903, the year of Whitney's paper, a discussion of corrosion appeared in Volume III of the TRANSACTIONS by C. J. Reed, entitled "Protective Action of Zinc Chloride on Iron" in which the introduction contained the following statement: "It is now generally recognized that the rusting or oxidation of metallic iron in the presence of water and saline solutions is an electrochemical process, the water or saline solution being the electrolyte and the metallic iron the anode. Small particles of graphitic carbon and other impurities or alloys serve as cathode to form local electrolytic circuits." Volume III contained, in addition, papers on the corrosion of metals by electrolysis, and the corrosion of aluminum, with discussion of stray current corrosion and cathodic protection using sacrificial anodes. In fact, it appears that by 1900, the practical use of zinc to protect boilers, condenser tubes, and ships was well established, even though the principles were not as yet fully understood. One discussion of that day mentioned a copper-plated steel ship badly corroded along damaged areas, for stated reasons that are acceptable today. Mention was also made of aluminum hulls corroded by stray current and of aluminum plates that failed, fastened by iron rivets to a manganese-bronze hull.

The announcement of corrosion as an electrochemical process probably came as no great surprise to charter members of the Society. The general relationship of corrosion to electrochemistry was suspected by several electrochemists of that period and was recognized in at least a qualitative way. Whitney's main contribution was a clear formulation of the theory, tying in the new facts of physical chemistry then originating from European laboratories headed by Ostwald, Arrhenius, and Nernst. Also, Caspari (1899) had just described hydrogen overvoltage for the first time, and Whitney included recognition of this phenomenon in his theory, although he did not mention it by name. W. H. Wollaston as early as 1801, had implied in a paper published in the *British Philosophical Magazine* that corrosion was electrochemical, and in 1830 de la Rive in France made quite clear that the corrosion rate of zinc depended on cathodic impurities and on the conductivity of electrolyte. In fact, just before Whitney's paper appeared, Ericson-Aurén and Palmaer of Sweden, published in 1901 to 1903, papers on the electrochemical corrosion of zinc. Also in 1900, a brilliant senior thesis by Carl Hambuechen appeared in the *Bulletin* of the University of Wisconsin on the electrochemical nature of the corrosion of iron, a paper that somehow has been completely neglected in the corrosion literature. But it was Whitney's paper above all others that persuaded many other workers that corrosion held interest as an important electrochemical process. It was also timed just about right to answer questions which engineers of that period raised concerning hope of alleviating the slow, inevitable disintegration of equipment, machinery, and structures then being made of metals on a large scale.

One of the men stimulated by Whitney's paper was Professor W. H. Walker who founded at Massachusetts Institute of Technology the first department of chemical engineering in this country. Walker and his students studied the effects of dissolved oxygen as a cathodic depolarizer of corrosion cells, and showed that the corrosion rate of iron was proportional to dissolved oxygen concentration. It was this work which led to the proposal of vacuum deaeration for corrosion control, and which pointed to one of the major means for protecting steam boilers from corrosion. Walker also proved that carbonic acid was not essential to initiate corrosion, contrary to strong ideas held by some at that time. But, while Walker and others were making significant contributions to the subject on the basis of the electrochemical theory, a number of papers appeared in England opposing the ideas of Whitney and proposing instead that corrosion was a direct chemical reaction involving either peroxides or colloids. This fruitless discussion continued into the early 1920's when the overwhelming evidence in favor of the electrochemical theory pushed the opposition into obscurity.

The expanding use of steel for buried structures, vibrating machinery, high-temperature applications, and high-velocity liquids brought recognition that corrosion could appear in forms other than rusting or pitting. Between 1910 and 1920, papers appeared describing microbiological corrosion, corrosion fatigue, stress corrosion cracking (caustic embrittlement), and cavitation. G. Tammann of Göttingen announced in 1920–22 the parabolic and logarithmic equations for tarnish and high-temperature oxidation of metals. About 10 years later, C. Wagner showed that this type of corrosion was also electrochemical in nature, the responsible cells differing in detail from those operating in aqueous corrosion.

By 1920, considerable work had started both in this country and abroad on various phases of corrosion as affecting not only ferrous but also nonferrous metals. The Research Laboratory of Applied Chemistry at Massachusetts Institute of Technology at this time began a series of studies on the fundamentals of corrosion supported in part directly, and for the first time, by industry. It was this research, along with parallel work elsewhere, that marked the beginnings of corrosion engineering. It also stimulated in some measure the publication of "Corrosion, Causes and Prevention" by Frank N. Speller, who acted as liaison for the National Tube Company, then major sponsor of the M. I. T. corrosion research. Meanwhile, convincing quantitative fundamental data were accumulating in England, and the science of corrosion was introduced as a challenging field of study. U. R. Evans' book, "The Corrosion of Metals," published in 1924 and his later volume, "Metallic Corrosion, Passivity and Protection," were especially influential in this regard. In 1936, the first

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volume of "Korrosion Metallischer Werkstoffe" appeared by Bauer, Kröhnke, and Masing summarizing among other data the early fundamental investigations of corrosion by Heyn and Bauer (1908) in Germany. Also in 1936, McKay and Worthington made available their "Corrosion Resistance of Metals and Alloys" which was especially welcomed by the active, growing field of chemical engineering. Three years later, Burns and Schuh published their valuable book on "Protective Coatings for Metals." The corrosion literature by this time had grown to sizeable proportions, indicating an expanding interest in the subject by industry and by those in research.

The use of chromates as possible inhibitors was announced by Dunstan, Jowett, and Goulding in the *Journal of the Chemical Society* for 1905. Cathodic protection in the form of sacrificial anodes or as sacrificial coatings was in common use when the Society was first founded, as mentioned earlier, but the use of applied currents for this purpose was apparently first tried in England in 1910 and in this country in 1912. Today, cathodic protection represents a major approach to corrosion control, and, as a new technology, accounts for the employment in this country of engineers in the hundreds and auxilliary personnel in the thousands. Hot-water vacuum deaeration was first described by W. H. Walker in Volume 14 of the TRANSACTIONS in 1908. This same year, zinc chromate pigments were described in *Science* by A. S. Cushman.

The stainless steels appeared on the market in the early 1920's followed by several of the corrosion-resistant alloys so familiar to chemical engineers today. Earlier, aluminum-bronze, Admiralty metal, Monel, and silicon cast iron were described and were at least in limited use. The tremendous advances in the corrosion-resistant alloy field in recent years requires no elaboration.

Corrosion testing in this country began soon after organization of the Society. In 1906, A.S.T.M. organized Committee A-5 to conduct fact-finding service tests on ferrous materials. Many other types of service tests followed. The important soil corrosion studies of the National Bureau of Standards were begun in 1922. In 1935, the Kure Beach Marine Test Station of the International Nickel Company, Inc., was established near Wilmington, North Carolina. With present expanded facilities at Harbor Island, this has now become perhaps the largest marine corrosion test station in the world.

In more recent years, the increasing awareness of industry of its concern with corrosion problems has led to the establishing of industrial corrosion laboratories, some of which have made major contributions to our present knowledge of the subject. Corrosion laboratories have been established, for example, by Aluminum Company of America, The International Nickel Company, Shell Development Company and several other oil companies, Bell Telephone Laboratories, DuPont, Battelle Memorial Institute, Dow Chemical Company, and Aluminum Company of Canada, Ltd.

A marked stimulus to corrosion research was provided by the emergencies of World War II. The Armed Services became acutely aware of corrosion and its importance, especially as equipment ranging from delicate electronic instruments to machine gun parts rapidly failed in shipment across the oceans or in the corrosive atmospheres of the tropical regions. It was this situation that led to much of the current fundamental research in corrosion at various university laboratories sponsored in major part by the Office of Naval Research and to a lesser extent by other branches of the Armed Services and by industry.

Although interest in corrosion by the Society was maintained from the very beginning, the growing importance of this field was finally expressed by organization of the Corrosion Division in 1942. In addition to holding annual symposia one of the first accomplishements of the Division was publication of the "Corrosion Handbook" in 1948. The wide sales of this book here and abroad have done much to cement the strong link which exists between corrosion and the Society's interests. The Corrosion Division is now one of the strongest in the Society both in membership and papers published.

The National Association of Corrosion Engineers was founded in 1945 and has presently a membership of over 3000 indicating an impressive growth of corrosion engineering. When N.A.C.E. was first organized, it was agreed between the officers of the Corrosion Division and the officers of the Association that engineering papers would be steered largely toward publications of the Association, whereas fundamental papers would be submitted to and published by the Society.

With the present pronounced trend toward conservation of our national resources and with industry even more keenly interested in prolonging the life of equipment and structures, the subject of corrosion has gained a mature status in civic, federal, and industrial planning. The corrosion engineer and corrosion scientist in addition to serving industry have proved their value to the world's economic well-being and future survival.

The Electrochemical Society can take pride in the role it assumed very early in the development of corrosion, which it now continues as a conspicuous part of its activities and services.

GENERAL REFERENCES

1. WILSON LYNES, "Some Historical Developments Relating to Corrosion," *J. Electrochem. Soc.*, **98**, 3*C* (1951).
2. F. N. SPELLER, "Corrosion Research and Abatement—Yesterday and Today," *Corrosion*, **1**, 1 (1945).
3. F. N. SPELLER, "Reminiscences of Early Corrosion Research," *Corrosion and Material Protect.*, **3**, 6 (1946).
4. W. BANCROFT, *J. Phys. Chem.*, **28**, 785 (1924).

Feature Section

OLIVER PATTERSON WATTS

Pioneer Teacher of Electrochemistry

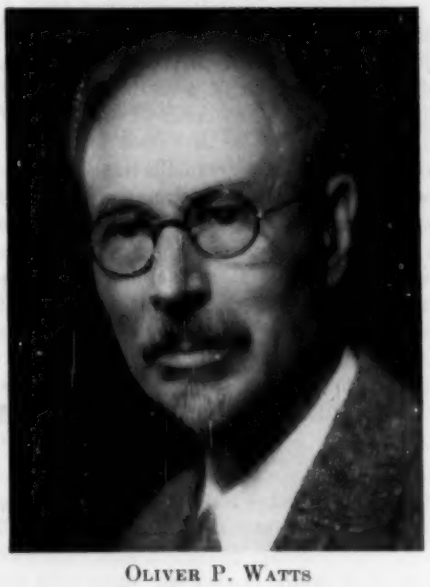
*O. A. Hougen**

On this golden anniversary of The Electrochemical Society, it is fitting that this Society pay special tribute to Oliver Patterson Watts, the dean of professors of applied electrochemistry in the United States, who has made scientific contributions to the Society for these fifty years and was its Vice-President in 1926 and 1927. Despite his eighty-seven years Dr. Watts is still to be found in his small laboratory actively engaged daily in experiments on corrosion and electroplating. Never has he abandoned laboratory work and personal experimentation for desk work. His direction of students in experimentation and research has always been by demonstrations in the laboratory through his own personal manipulations.

To Dr. Watts, exploring the complex problems of electrochemistry and corrosion has been a work of love and devotion. Reliance upon experimentation and an attempt to find the answers which nature provides have always preceded any acceptance of results formulated by the extrapolation of mathematical equations. In the classroom Watts has insistently stressed the ability to think and to explain by scientific reasoning, and has demanded full scientific explanations for all answers without depending upon statements memorized from textbooks. Dr. Watts belongs to the small group of scientists who are always distinguished as such by appearance and behavior. There is no mistaking him for other than a distinguished and scholarly scientist.

Oliver Patterson Watts was born in Thomaston, Maine, July 16, 1865, the son of Joseph B. and Maria Patterson Watts. Following his graduation from Bowdoin College in 1889 and one year of graduate studies at Clarke University of Worcester, Massachusetts, he taught as a principal of the grammar school in his home town of Thomaston, for two years. After this, he taught chemistry and physics for six years in Franklin Academy and for five years in the city high school at Waltham, Massachusetts.

While at Waltham he became interested in the great developments in applied electrochemistry which were then receiving major attention on the part of those developing the chemical industry of the United States. In 1898, a department of Applied Electrochemistry had been established at the University of Wisconsin by Professor Charles F. Burgess. Accordingly, in 1902 Watts went to the University of Wisconsin to study electrochemistry under Professors Burgess and Louis Kahlenberg and received, in 1905, the first doctorate degree offered by the departments of electrochemistry or chemical engineering. His thesis was entitled, "An Investigation of the Borides and Silicides." In the same year the Trustees of the Carnegie Institution of Washington established a research grant of $2500 a year for a period of five years "to investigate the properties of electrolytic iron and its alloys." This project was assigned to Dr. Watts for direction and performance. In the fall of 1905 the department of chemical engineering was established at Wisconsin and the department of applied electrochemistry was merged with it.



OLIVER P. WATTS

Watts remained as an instructor and professor in applied electrochemistry until the time of his retirement in 1937 and since then has continued up to the present in solitary laboratory experimentation without any salary or compensation beyond the love of finding out for himself the answers which nature will always provide to those who search diligently and with an inquiring mind.

Watts' first wife, Mary J. Orton, the daughter of President Edward Orton of Ohio State University, was his devoted and inspiring companion until her death some years after his retirement. In 1948 he married Estella Nuzum Jones who has been the faithful helpmate of his later years.

The list of "Conundrums in Corrosion" published herewith represents the inquiring approach which Watts always pursued in his teaching methods, constantly prodding the students to give answers based upon profound and sustained scientific thinking from premise to premise without relinquishing the thought pattern until an answer was obtained by rigid inquiry rather than from memorized statements.

The scientific works of Dr. Watts, of which 31 papers

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appear in the TRANSACTIONS of the Society, include the general theories and applications of electrochemistry, rates of corrosion, the rusting of iron, the effects of dissolved oxygen and water line on corrosion, the grading of corrosion-resisting alloys, the behavior of voltaic couples; in electroplating, the problems of embrittlement, dezincification, structure of electrodeposits, and the effect of addition agents. In electrometallurgy Watts early investigated the production of calcium carbide, carborundum, the borides, silicides and nitrides of metals, and hundreds of alloys. In 1924 he received the honorary degree of Doctor of Science from his alma mater, Bowdoin College.

Dr. Watts never concerned himself with financial rewards for his endeavors. His consulting services were given without thought of compensation. His development of the hot nickel-plating bath, now used throughout the world and universally known as the "Watts Bath," has been repeatedly declared to have earned millions of dollars for the plating industry. It brought him no monetary compensation. The following statement has been taken from the biography of Charles F. Burgess by Alexander McQueen, entitled "A Romance in Research."

> "Early in 1913 the Chicago branch of the National Electro-Platers Association notified Burgess that he and Dr. O. P. Watts had been elected honorary members of the branch. This friendly gesture was prized highly, because these electroplaters were practical men in the shops, and their action proved that they recognized the value of scientific research as applied to the processes of their work. Soon afterwards the National Electro-Platers Association became the American Electro-Platers Society, and again Burgess and Watts received honorary membership, this time nation-wide, in the new organization. They shared the honor with several other prominent men, including Burgess's old acquaintance Professor Joseph W. Richards, of Lehigh, and Dr. George F. Kunz of Tiffany and Co., write[r] of many books on the lore of precious stones. Burgess [a]nd Watts never lost touch with progress in the electroplating field and Watts earned the lasting gratitude of the trade by working out an improved high-speed method of nickel plating on iron and steel which is still known as the Watts Bath."

A wise choice and use of hobbies are good reasons for a long and active life. Watts has always been fond of the out-of-doors. Until his retirement at the age of seventy, Dr. and Mrs. Watts continued to spend their summers sailing along the coast of Maine. His sloop, Kestrel, was an able and comfortable boat, thirty-one feet in length, with a cabin providing full head room, "as able and comfortable for her size as any boat ever put together. In speed only racing boats could pull away from the Kestrel when the breeze was good." Nearly every summer Dr. and Mrs. Watts sailed the entire Maine Coast out of his beloved Thomaston, with never an envy for the finest yacht in their company. After retirement the Watts toured by car, with tent and camping outfits, the entire United States and Canada on their summer trips, even penetrating the rough roads leading into the Northwest Territory of Canada. At the age of eighty, Watts purchased a new-fangled pair of shoe skates to replace the old detachables which had served him for sixty years. In recent years Dr. Watts and his present wife have spent their winters in Florida away from the extremes of Wisconsin winters. Photography and astronomy have also been lifelong hobbies, and a source of entertainment for his students and guests.

Dr. Watts is one of the survivors of that school of rugged individualists in applied science who has persisted in his own unaided investigational efforts. He is responsible for the emphasis on applied electrochemistry in the Department of Chemical Engineering at Wisconsin and has been a source of inspiration to hundreds of students in his classes.

Conundrums in Corrosion[1]

Oliver P. Watts

Professor Emeritus of Chemical Engineering, University of Wisconsin, Madison, Wisconsin

I. A thin sheet of copper is weighed, suspended vertically in a dilute solution of sulfuric acid in contact with air, and connected through a sensitive milliammeter to a similar sheet of platinum, each 1 dm^2. The copper will corrode, and hydrogen will be displaced invisibly on the platinum and removed by combination with oxygen dissolved from the air.

Will the weight of copper dissolved in a period of two months exceed, be equal to, or be less than the amount computed by Faraday's law from the number of ampere-hours of current flowing?

Will any of the dissolved copper be deposited on the platinum cathode by the current?

II. Two sheets of iron and copper of equal area are similarly connected in a solution containing 35 grams of sodium chloride, and 70 grams of sodium citrate per liter. Air is bubbled through the solution to serve as a depolarizer for hydrogen.

How will the corrosion of iron compare with the amount calculated from the current flow? How will the weight of copper cathode be affected? Explain.

III. A copper-platinum couple is immersed in an acid-copper sulfate solution in contact with air. What happens at the platinum cathode? Explain.

IV. The potential of platinum is 0.7 volts below that of copper in a dilute solution of sulfuric acid. Will the removal of all dissolved air and oxygen from the solution and the prevention of its depolarizing action at the cathode result in the deposition of copper on the platinum? Explain.

V. What is the mechanism of the sulfation (loss of charge) of the lead plates of the starting battery of your car on long idle standing? Is it due to the (*a*) direct union of the lead with the SO_4 ion of the dissociated H_2SO_4? (*b*) corrosion by oxygen depolarization? Would this corrosion cease by removing and excluding all dissolved oxygen from the electrolyte? (*c*) displacement of hydrogen from the acid at so slow a rate that the hydrogen can diffuse to the liquid surface and escape unseen?

VI. Equal sheets of iron are immersed in the following solutions: (*a*) sodium chloride; (*b*) sodium chloride, with addition of sodium citrate to force back the dissociation of the chloride by the common-ion effect.

Does the addition of the sodium citrate increase or diminish the rate of corrosion?

[1] In these provocative questions Emeritus Professor Oliver P. Watts solicits your answers in writing, addressed to his home at 114 N. Spooner Street, Madison, Wisconsin. As far as possible the correct answers will be published later.

VII. When a sheet of copper is submerged between equal sized sheets of silver and platinum in dilute sulfuric acid, and the three are connected electrically, copper dissolves and displaces hydrogen on both cathodes. Each cathode is polarized up to the potential of copper and the amount of polarizing hydrogen is greater on the platinum than on the silver. If corrosion proceeds by oxygen depolarization, will the currents flowing between the individual cathodes and the anode be equal or different?

VIII. Can contact with copper ever slow down or prevent the corrosion of iron in any electrolyte open to the air?

IX. For the same total metal surface, is corrosion by oxygen depolarization greater when two-thirds of that surface is furnished by the anode or by the cathode? For example, in an electrolyte of ammonium sulfate acidified by sulfuric acid, couple A consists of two sheets of copper, 5 cm², with a single sheet of silver of the same dimensions midway between the two copper sheets; and the three sheets are connected by wire. Couple B consists of two silver sheets with a single copper sheet midway between.

Is corrosion greater in A or B at the end of two months? Explain.

X. In the case of one metal protecting another by contact in an aqueous solution, the more active metal protects the other by substituting its own corrosion for that of the other metal. (*a*) Suppose the active metal is put in electrical contact with a metal which is not subject to corrosion in that particular electrolyte. Will this contact stimulate corrosion of the active metal to the same degree as does contact with a corrodible metal, which the active metal must then protect by its own corrosion? (*b*) How about the relative stimulation of the corrosion of iron by contact with equal sheets of silver and platinum, when there is no visible displacement of hydrogen either before or after contact with the other metal?

XI. Two copper-platinum couples, A and B, are immersed in separate beakers in 200 cc of dilute sulfuric acid for seven hours. To beaker B, 24 grams of ferric chloride was added as a depolarizer, and current readings were made at 15-minute intervals.

The current in B averaged 16 times that in A, but corrosion in B was 23 times that in A. Explain this excessive corrosion.

XII. Two different cells are connected in opposition. The cells Fe-Cu and Ag-Fe, in a solution of ammonium sulfate plus ammonium citrate, are connected, iron to iron, and silver to copper, for 22 days. What changes occur and where?

XIII. Equal sheets of iron and copper, 5 cm², are supported vertically for nine days in the following solutions: the copper in a liter of water containing 10 cc of concentrated sulfuric acid, the iron in a liter of water containing 20 grams of ammonium chloride and 40 grams of ammonium citrate. Air is slowly bubbled up back of each electrode, for its stirring effect, and to maintain the air content of the electrolytes. Which metal wins this corrosion Derby, the copper in the acid electrolyte, or the iron in the neutral solution? Why so?

XIV. Two closely fitting disks of sheet copper are immersed in a tall tumbler filled with dilute sulfuric acid, from which the air has been removed by application of a vacuum. The copper disks are placed horizontally, one at the bottom, the other near the upper surface of the solution. When connected by a wire there is a microscopic flow of current from the lower to the upper electrode; but after several months the cathode had lost more weight than the anode! Explain.

XV. Sheet copper is immersed in an air-free solution of copper sulfate. Will copper corrode or be deposited?

XVI. Two small beakers are filled with acid copper-sulfate plating solution. Copper electrodes, 2.54 cm by 3.81 cm, are placed in one beaker and a copper anode and platinum cathode in the other. A current of 0.10 milliamperes is sent through the two cells connected in series for thirty days. The total current flowing is 0.072 ampere-hours, equivalent to 85 milligrams of copper. There is no copper deposit on the platinum. Why not?

XVII. In two similar rectangular jars each holding 1200 cc of electrolyte and exposing 90 cm² of surface to the air, the couples Cu-Pt and Fe-Cu with electrodes, 1 dm², were immersed for 30 days. Cell A, with the copper anode, contained 90 cc of concentrated sulfuric acid, and cell B, with the iron anode, contained 84 grams ammonium chloride and 72 grams ammonium citrate. The citrate was added to maintain a clean surface on the iron and give it a fair chance in this corrosion contest. Which couple won this corrosion Derby? Why?

XVIII. A cylindrical dish 21 cm in diameter is filled with a solution of 70 grams ammonium citrate and 50 grams ammonium chloride and a few drops of formalin in four liters of water. A couple consisting of sheet iron and silver each 1 dm² is immersed at one side of the dish, and a bar of cadmium is electrically connected to the iron. The electric current which flowed from iron to silver varied between 1.3 and 0.7 milliamperes during 19 days. There was no corrosion of the iron, although 0.4 ampere-hour total current had passed from iron to silver through the electrolyte. Explain the failure of the iron to corrode.

XIX. In plating from an acid copper sulfate plating solution no hydrogen is seen; but from a cyanide copper plating solution, evolution of hydrogen accompanies the deposition of copper. Why does this difference appear?

XX. A copper-platinum couple of sheets one dm square is immersed in a strong solution of copper sulfate, acidified by sulfuric acid. For four days a current of 0.7 to 0.8 milliamperes flowed from the copper to the platinum without visible deposition of either hydrogen or copper on the platinum. Explain.

Photo: Courtesy of Henry Vogt Machine Co., Louisville, Ky.

ONE OF BRIDGEPORT'S CONDENSER TUBE ALLOYS MAY SOLVE YOUR CORROSION PROBLEMS

No one metal or alloy can be expected to withstand the many different corrosive elements encountered in chemical plants, petroleum refineries and food processing industries. Bridgeport has developed a number of condenser tube alloys designed to meet a wide range of operating conditions. Selection of the tubing best suited for a particular application requires considerable experience and knowledge. Bridgeport maintains a consistent program of corrosion research involving laboratory work as well as field and service tests. Contact the nearest Bridgeport office for technical service to help reduce premature tube failures, and write for 112-page Condenser Tube Manual.

ARSENICAL ADMIRALTY—for handling sea water or polluted fresh circulating water, hydrocarbon gases containing sulfur compounds, lubricating oils, gasoline, naphtha, etc.

ARSENICAL MUNTZ*—excellent for resisting high sulfur compounds as well as dezincification from corrosive water. More effective than ordinary Muntz.

CUZINAL—superior to Admiralty for resisting air impingement corrosion or erosion-corrosion produced by high water velocities. Resists dezincification and sulphide corrosion encountered in condensers and coolers handling various types of petroleum products.

CUPRO NICKEL—resists stress corrosion cracking caused by moist ammonia, oxygen and stress. Shows good resistance to caustic and other alkaline liquids and salt solution. Fine resistance to air impingement corrosion produced by high sea water velocities.

RED BRASS—resists corrosive waters and hydrocarbon vapors. Better for resisting stress corrosion than Admiralty or Cuzinal, but not recommended for severe sulfur corrosion.

DURONZE IV**—excellent for circulating sea water and brackish waters polluted with wastes. Gives fine service conducting hot brine in salt refineries and corrosive liquids in many processing plants.

DUPLEX TUBING—for double corrosive conditions too severe for single metal or alloy—extensively used in ammonia refrigeration systems and heat exchangers and condensers handling a wide variety of organic and inorganic chemicals. Available in Red Brass, Copper, Cuzinal, Cupro Nickel, Muntz, and Duronze IV . . . with steel, aluminum, stainless or monel. Inner and outer tubes are selected to combat a specific corrosive element and mechanically combined to give good heat transfer. Our Technical Bulletin No. 746 covers applications and methods of installing Duplex Tubing.

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Current Affairs

Program for the Montreal Meeting

Completed arrangements for the Montreal Meeting of the Society, which will take place on October 26–30, present a gratifying program of technical sessions, plant trips, and social events that is sure to stimulate wide interest. General Chairman A. W. Whitaker and the various committee members and chairmen have, in addition to planning a well-rounded schedule, given the meeting some unusual and interesting features.

Headquarters for the meeting is the Sheraton-Mount Royal Hotel, located at Peel and St. Catherine Streets. Registration will begin on Sunday, October 26, and will be held on the Mezzanine floor.

With reference to plant trips, members are requested to note carefully the directions for making reservations for the Arvida trip (see September JOURNAL and Program Booklet).

In addition to the Battery—Electric Insulation Round Table on "Battery Separators," on October 28 at 2:00 P.M., there will be an Electrothermics Round-Table discussion on October 29 at 9:00 A.M. on "The Electrothermic Industries in Canada and Their Relationship to the Future Requirements of the United States and Canada."

Immigration and Customs

American citizens entering Canada should carry adequate proof of citizenship, such as a passport, birth certificate, or comparable documents of identification. Non-citizen residents of the U. S. are advised to check in advance with immigration authorities, since the requirements vary with the circumstances of individual cases.

Canadian Customs—Gifts may be brought into Canada, duty free, up to the value of $10.00, except gifts of tobacco or liquor. Visitors may bring in a limited supply of tobacco or liquor for their own use together with their personal effects.

Canadian Customs will grant temporary permits for importation of cameras, typewriters, radios, etc. These items, of course, must return with the visitor when he leaves.

U. S. Customs—After a stay of 48 hours, American visitors may return with goods up to $200.00 value, free of duty, with certain reservations.

Technical Program

Monday, October 27, 1952

9:00 A.M.—Formal Opening of the 102nd Convention with Introduction by General Chairman A. W. Whitaker, Jr., and response by President J. C. Warner.

Batteries

Wednesday, October 29, 1952

Primary Cells

J. N. Mrgudich presiding

9:00 A.M.—"The Potential and Coulombic Capacity of Some Galvanic Cell Systems" by Allan Walkley, Minerals Utilization Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.

9:20 A.M.—"The Reproducibility of the Manganese Dioxide Electrode and the Change of Electrode Potential with *pH*" by Richard S. Johnson, National Carbon Research Laboratories, Cleveland, Ohio, and W. C. Vosburgh, Department of Chemistry, Duke University, Durham, N. C.

9:40 A.M.—"A High Voltage Pile of the Zamboni Type" by Paul L. Howard, National Bureau of Standards, Washington, D. C.

10:10 A.M.—"Structural Properties of Some Synthetically Prepared Manganese Dioxides" by G. Butler and H. R. Thirsk, Physical Chemistry Laboratory, University of Durham, King's College, Newcastle-upon-Tyne, England.

10:30 A.M.—"The Situs of Depolarizing Reaction in the Dry Cell" by Shiro Matsuno, Yuasa Dry Battery Company, Ltd., Takatsuki, Osaka, Japan.

10:50 A.M.—"Use of Solid Semiconductors as Ion Carriers in Electrochemical Systems" by K. Lehovec and J. Broder, Squier Signal Laboratory, Signal Corps Engineering Laboratories, Fort Monmouth, N. J.

Batteries (cont'd.)

Secondary Batteries

E. Willihnganz presiding

2:30 P.M.—"Preparation of High Purity Lead" by Ray C. Hughes, Philips Laboratories, Inc., Irvington on Hudson, N. Y.

2:50 P.M.—"Positive-Plate Self-Discharge in the Lead-Acid Cell" by J. J. Lander, Naval Research Laboratory, Washington, D. C.

3:10 P.M.—"Microsegregation in the Lead-Antimony Alloys" by A. C. Simon and E. L. Jones, Naval Research Laboratory, Washington, D. C.

3:30 P.M.—"Effect of Corrosion and Growth on the Life of Positive Grids in the Lead-Acid Cell" by J. J. Lander, Naval Research Laboratory, Washington, D. C.

3:50 P.M.—"Impedance Measurements in Storage Batteries" by E. Willihnganz, Gould-National Batteries, Inc., Depew, N. Y.

4:10 P.M.—"Mechanism of Self-Discharge in the Edison Negative" by P. Hersch, The Mond Nickel Company, Ltd., Development and Research Department, Birmingham, England.

4:30 P.M.—"The Relation of the Anodic Corrosion of Lead and Lead-Antimony Alloys to Microstructure" by J. B. Burbank and A. C. Simon, U. S. Naval Research Laboratory, Washington, D. C.

Joint Session

Battery—Electric Insulation

Tuesday October 28, 1952

Round-Table Discussion

Battery Separators

Harold C. Beachell presiding

2:00 P.M.—The purpose of the round table is to bring together battery and insulation specialists to exchange ideas on battery separator problems in an effort to resolve some of the problems of mutual interest.

The following will act as discussion leaders in various phases of this topic: E. Willihnganz, V. S. Harris, W. Shorr, and A. J. Salkind.

Corrosion

Monday, October 27, 1952

Harry R. Copson presiding

9:15 A.M.—"The Oxidation of Metals at High Temperatures" by Walter J. Moore, H. H. Wills Physical Laboratory, University of Bristol, Bristol, England.

9:45 A.M.—"Theoretical Analysis of the Diffusion Processes Determining the Oxidation Rate of Alloys" by Carl Wagner, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

10:15 A.M.—"Oxidation Studies on Pure Nickel from 400° to 750°C and at Pressures from 0.76 to 76.0 mm of Hg of O_2" by Kenneth F. Andrew and Earl A. Gulbransen, Westinghouse Research Laboratories, East Pittsburgh, Pa.

10:45 A.M.—"A Preliminary Study of the Oxidation and Vapor Pressure of Chromium" by Earl A. Gulbransen and Kenneth F. Andrew, Westinghouse Research Laboratories, East Pittsburgh, Pa.

11:15 A.M.—"The Reaction of Zirconium Metal Surfaces with Oxygen" by M. W. Mallett, H. R. Nelson, and C. A. Papp, Battelle Memorial Institute, Columbus, Ohio.

11:45 A.M.—"The Reaction of Nitrogen with Beta Zirconium and the Diffusion and Solubility of Nitrogen in the Metal" by M. W. Mallett, E. M. Baroody, H. R. Nelson, and C. A. Papp, Battelle Memorial Institute, Columbus, Ohio.

2:00 P.M.—"High Temperature Corrosion of Several Heat Resisting Alloys by Anhydrous Ammonia" by E. N. Skinner, Jr., Development and Research Division, The International Nickel Company, Inc., New York, N. Y., and D. E. Furman, Research Laboratory, The International Nickel Company, Inc., Bayonne, N. J.

2:30 P.M.—"The Accelerated Oxidation of Alloy Steels in Contact with Vanadium Pentoxide at High Temperatures" by H. H. Marvin and H. A. Liebhafsky, Research Laboratory, General Electric Company, Schenectady, N. Y.

3:00 P.M.—"Effect of Copper Contamination on Two Cast Heat Resisting Compositions" by G. F. Geiger, Development and Research Division, International Nickel Company, Inc., New York, N. Y., and A. M. Talbot, Research Laboratory, International Nickel Company, Inc., Bayonne, N. J.

3:30 P.M.—"Corrosion of Heating Electrodes in Molten Chloride Baths" by H. R. Copson, Research Laboratory, International Nickel Company, Inc., Bayonne, N. J.

4:00 P.M.—"Aqueous Corrosion of 2S Aluminum at Elevated Temperatures" by J. E. Draley, Argonne National Laboratory, Chicago, Ill.

4:30 P.M.—"Corrosion of Zirconium in High Temperature Water" by A. H. Roebuck, J. E. Draley, and C. R. Breden, Argonne National Laboratory, Chicago, Ill.

5:00 P.M.—"Kinetics of Reactions of Nickel and Steel with Molten Sulfur" by Andrew Dravnieks, Standard Oil Company (Indiana), Chicago, Ill.

Tuesday, October 28, 1952

Corrosion (cont'd.)

Harry R. Copson presiding

9:00 A.M.—"Some Problems in Corrosion Research" by Owe Berg, Avesta Jernverks Aktiebolag, Avesta, Sweden.

9:30 A.M.—"Corrosion of Steel by Air-Free, Dilute, Weak Acids" by Norman Hackerman and E. E. Glenn, Jr., University of Texas, Austin, Texas.

10:00 A.M.—"The Anodizing of Zirconium and Other Transition Metals in Nitric Acid" by R. D. Misch and W. E. Ruther, Argonne National Laboratory, Chicago, Ill.

10:30 A.M.—"Kinetics of the Oxidation and Dissolution of Copper in Aqueous Ammonia" by J. Halpern, Department of Metallurgy, University of British Columbia, Vancouver, Canada.

11:00 A.M.—"Time-Dependent Properties of Copper Anodes in HCl Solutions" by J. H. Bartlett and L. P. Stephenson, Physics Department, University of Illinois, Urbana, Ill

11:30 A.M.—"Corrosion of Mild Steel Sheet in 6N Hydrochloric Acid at 90°C" by E. L. Koehler, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.

11:55 A.M.—"On the Repeated Etching and Electrolytical Polishing of Metals" by Shigeto Yamaguchi, Scientific Research Institute, Ltd., Tokyo, Japan.

11:57 A.M.—"On Visual Determination of the Orientation and Non-orientation of Crystallites Composing Thin Films" by Shigeto Yamaguchi and Tadayuki Nakayama, Scientific Research Institute, Ltd., Tokyo, Japan.

2:00 P.M.—"Corrosion of Aluminum in Nonaqueous Nitric Acid and Mixed Nitric-Sulfuric Acid Media" by Milton D. Scheer and Eric Rau, U. S. Naval Air Rocket Test Station, Dover, N. J.

2:30 P.M.—"The Rate of Dissolution of Titanium in Acids with Ammonium Fluoride Added" by M. E. Straumanis and C. B. Gill, School of Mines and Metallurgy, University of Missouri, Rolla, Mo.

3:00 P.M.—"Passivity of Titanium in Hydrochloric Acid Solutions" by David Schlain, U. S. Bureau of Mines, College Park, Md., and Joseph S. Smatko, University of Maryland, College Park, Md.

3:30 P.M.—"Amount of Oxygen on the Surface of Passive Stainless Steel" by Herbert H. Uhlig and Samuel S. Lord, Jr., Corrosion Laboratory, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

4:00 P.M.—"Inorganic Corrosion Inhibitors in Acid Solution" by Cecil V. King, Emil Goldschmidt and Natalie Mayer, Department of Chemistry, New York University, New York, N. Y.

4:30 P.M.—"The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors" by M. J. Pryor and M. Cohen, National Research Council, Ottawa, Canada.

Electric Insulation

Tuesday, October 28, 1952

The Physics and Chemistry of Dielectrics

Harold C. Beachell presiding

9:00 A.M.—"The Manufacture, Properties, and Uses of Formvar" by Andrew F. Fitzhugh and Edward Lavin, Shawinigan Resins Corporation, Springfield, Mass., and George O.

Morrison, Shawinigan Products Corporation, New York, N. Y.

9:30 A.M.—"Infrared Absorption Spectra of Polyvinyl Formal" by Harold C. Beachell, Department of Chemistry, University of Delaware, Newark, Del.

10:00 A.M.—"Electrical Properties of Araldite Ethoxyline Resins" by M. Wismer and E. N. Dorman, Ciba Company, Inc., New York, N. Y.

10:30 A.M.—"The Pulse-Breakdown of Liquids" by W. D. Edwards, National Research Council, Ottawa, Canada.

11:00 A.M.—"Insulation Problems in Nuclear Measurements" by Wendel H. Bradley, Nuclear Measurements Corporation, Indianapolis, Ind.

11:30 A.M.—"Effect of Radiation on Dielectrics" by A. J. Warner, Federal Telecommunications Laboratories, Nutley, N. J.

Round-Table Discussion

Battery Separators

2:00 P.M.—Joint session, Electric Insulation and Battery Divisions (see Batteries).

Electrodeposition

Monday, October 27, 1952

Deposition and Polishing of Copper

R. A. Woofter presiding

9:20 A.M.—Opening Remarks.

9:30 A.M.—"Electrodeposition of Copper from the Monoethanolamine Bath" by T. L. Rama Char and N. B. Shivaraman, Electrochemistry Laboratory, Indian Institute of Science, Bangalore, India.

10:00 A.M.—"Studies of the Mechanism of Bright Plating in the Acid Copper Bath" by Bacon Ke and Dan Trivich, Department of Chemistry, Wayne University, Detroit, Mich.

10:30 A.M.—"The Electrodeposition of Copper and Nickel" by John Yeager, Ernest Yeager, and Frank Hovorka, Department of Chemistry, Western Reserve University, Cleveland, Ohio.

11:00 A.M.—"The Effect of Ultrasonic Waves on the Electrodeposition of Copper" by W. R. Wolfe, Hyman Chessin, Ernest Yeager, and Frank Hovorka, Department of Chemistry, Western Reserve University, Cleveland, Ohio.

11:30 A.M.—"A New Approach to the Investigation of Addition Agents" by B. I. Parsons and C. A. Winkler, Chemistry Department, McGill University, Montreal, Canada.

2:30 P.M.—"Cathode Polarization Potential during the Electrodeposition of Copper, III. Effect of the Cathode Base upon the Cathode Polarization Potential and the Crystal Structure of the Deposit" by L. L. Shreir, Battersea Polytechnic, London, England, and J. W. Smith, Bedford College, London, England.

3:00 P.M.—"The Mechanism of Surface Leveling by Periodic Reverse Current Cyanide Copper Plating" by Dennis R. Turner, Electroplating Projects Laboratory, Westinghouse Electric Corporation, East Pittsburgh, Pa.

3:30 P.M.—"The Mechanism of Electropolishing of Copper in Phosphoric Acid Solutions, I. Electrical Conditions Associated with Electropolishing" by J. Edwards, British Non-Ferrous Metals Research Association, London, England.

3:50 P.M.—"The Mechanism of Electropolishing of Copper in Phosphoric Acid Solutions, II. Processes Preceding the Establishment of Polishing Conditions" by J. Edwards, British Non-Ferrous Metals Research Association, London, England.

4:10 P.M.—"The Mechanism of Electropolishing of Copper in Phosphoric Acid Solutions, III. The Mechanism of Smoothing" by J. Edwards, British Non-Ferrous Metals Research Association, London, England.

4:30 P.M.—"Electronic Configuration in Electrodeposition from Aqueous Solutions, I. The Effect of Ionic Structure" by Ernest H. Lyons, Jr., The Principia College, Elsah, Ill.

Tuesday, October 28, 1952

Electroplating Processes

M. L. Holt presiding

9:00 A.M.—"Factors Affecting the Transformation of White to Gray Tin at Low Temperatures" by R. R. Rogers and J. F. Fydell, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

9:30 A.M.—"Electrodeposition of Selenium" by R. Scott Modjeska, Scientific Control Laboratories, Chicago, Ill., B. F. Freeber, Vapor Heating Corporation, Chicago, Ill., and Kurt E. Schimkus, S. & S. Laboratories, Chicago, Ill.

10:00 A.M.—"Electrodeposition of Silver from the Iodide Bath" by T. L. Rama Char and R. Sadagopachari, Electrochemistry Laboratory, Indian Institute of Science, Bangalore, India.

10:30 A.M.—"Some Properties of Stannous Sulfate Solutions and Their Role in Electrodeposition of Tin, II. Solutions with Stannous Sulfate and Sulfuric Acid Present" by C. A. Discher, College of Pharmacy, Rutgers University, Newark, N. J.

11:00 A.M. — "Electrodeposition of Cadmium from Fluoborate Solutions" by T. R. Anantharaman and J. Balachandra, Department of Metallurgy, Indian Institute of Science, Bangalore, India.

11:30 A.M.—"Electrogalvanizing from Fluoborate Solutions" by T. R. Anantharaman and J. Balachandra, Department of Metallurgy, Indian Institute of Science, Bangalore, India.

12:00 M.—"Cathodic Lead Disintegration and Hydride Formation" by Hugh W. Salzberg, Naval Research Laboratory, Washington, D. C.

Joint Session

Electrodeposition—Industrial Electrolytics

Wednesday, October 29, 1952

Electrowinning and Electrorefining of Metals

D. O. Hubbard and R. A. Woofter presiding

9:00 A.M.—"The Caustic Electrolytic Zinc Process" by Charles T. Baroch, R. V. Hilliard, and R. S. Lang, Bureau of Mines, U. S. Department of the Interior, Boulder City, Nev.

9:30 A.M.—"Development of a Canadian Source of Indium Metal" by J. R. Mills, B. G. Hunt, and G. H. Turner, The Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C., Canada.

10:00 A.M.—"The Electrorefining of Tin" by H. G. Poole, G. C. Ware, and F. Block, Bureau of Mines, U. S. Department of the Interior, Albany, Ore.

10:30 A.M.—"A Method for Introducing and Controlling the Concentration of Inorganic Addition Agents" by G. R. Van Houten, P. R. Mallory & Co., Inc., Indianapolis, Ind., and L. E. Stout, School of Engineering, Washington University, St. Louis, Mo.

11:00 A.M.—"Refining Antimony by Electrodeposition and by Vaporization" by R. R. Rogers and R. A. Campbell, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

11:30 A.M.—"Anodic Deposition Behavior of Manganese and Silver" by John T. Byrne, Dow Chemical Company, Rock Flats Plant, Denver, Colo., and L. B. Rogers, Department of Chemistry and Laboratory for

Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

Electrodeposition (cont'd.)

Wednesday, October 29, 1952

Plating of Unusual Metals

C. A. Snavely presiding

2:00 P.M.—"The Complete Electrodeposition of Radioruthenium" by J. C. Griess, Jr., Oak Ridge National Laboratory, Oak Ridge, Tenn.

2:30 P.M.—"A Study of the Electrodeposition of Ruthenium from Very Dilute Solutions" by M. H. Lietzke and J. C. Griess, Jr., Oak Ridge National Laboratory, Oak Ridge, Tenn.

3:00 P.M.—"Electroplating on Zirconium" by W. S. Schickner, John G. Beach, and Charles L. Faust, Battelle Memorial Institute, Columbus, Ohio.

3:30 P.M.—"Electroplating on Beryllium" by John G. Beach and Charles L. Faust, Battelle Memorial Institute, Columbus, Ohio.

4:00 P.M.—"Electroplating on Titanium" by William H. Colner, Morris Feinleib, and John N. Reding, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.

4:30 P.M.—"Formation of Immersion Zinc Coatings on Aluminum" by W. G. Zelley, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa.

Electrothermics

Round-Table Discussion

Wednesday, October 29, 1952

The Electrothermic Industries in Canada and Their Relationship to the Future Requirements of the United States and Canada

John Convey, Chairman

9:00 A.M.—The discussion will be introduced by panel members representing the electrothermic industries of Canada.

Industrial Electrolytics

Tuesday, October 28, 1952

D. O. Hubbard presiding

2:00 P.M.—"Determination of Current Efficiency by Gas Analysis Diaphragm Chlor Alkali Cells" by M. S. Kircher, H. R. Engle, B. H. Ritter, and A. H. Bartlett, Hooker Electrochemical Company, Niagara Falls, N. Y.

2:30 P.M.—"Influence of Impurities in the Electrolyte in Chlorine-Caustic Electrolysis by the Mercury Cell Process, III. Investigation of the Influence of Anions upon the Decomposition Rate of Sodium Amalgam" by Gösta Angel, Tage Lundén, and Rolf Brännland, Division of Applied Electrochemistry, Royal Institute of Technology, Stockholm, Sweden.

3:00 P.M.—"Influence of Impurities in the Electrolyte in Chlorine-Caustic Electrolysis by the Mercury Cell Process, IV. Description of a Mercury Cell Used for Electrolysis Experiments in Laboratory Scale" by Gösta Angel and Tage Lundén, Division of Applied Electrochemistry, Royal Institute of Technology, Stockholm, Sweden.

3:30 P.M.—"Graphite Anode in Brine Electrolysis, III. Effect of Anode and Operating Variables on Caustic Color" by M. Janes, N. J. Johnson, and E. B. Pilcher, Process Engineering Laboratory, National Carbon Company, Niagara Works, Niagara Falls, N. Y.

4:00 P.M.—"Electrical Conductivity of Molten Cryolite and Potassium, Sodium, and Lithium Chlorides" by Junius D. Edwards, Cyril S. Taylor, Allen S. Russell, and L. Frank Maranville, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa.

Joint Session

Industrial Electrolytics—Electrodeposition

Wednesday, October 29, 1952

Electrowinning and Electrorefining of Metals

D. O. Hubbard and R. A. Woofter presiding

9:00 A.M.–12:00 M.—For list of papers see Joint Session with Electrodeposition Division.

1952 Winners of Prize Essay Contest

The winners of the Prize Essay Contest, sponsored annually by The Electrochemical Society, have been selected and are announced by the Award Committee as follows:

First Prize—Gordon Gemmell, Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; *Second Prize*—Donald W. Hutchings, Grey Gables, East College Street, Oberlin, Ohio; *Honorable Mention*—Robert Auerbach, 347 East 173 Street, New York City.

The First Prize winner will be th recipient of a $100 cash award plus one-year membership in the Society the winner of the Second Prize wi receive a $50 cash award and a one-ye Society membership. The awards we given for the best essay (graduate undergraduate students), between 10 and 2000 words, on the subject "Th Electrochemical Nature of Corrosion."

The contest was established in 19 with financial support from income d rived from the "Corrosion Handbook."

National Research Corp. Joins Sustaining Member

The Society is pleased to announc the recent addition of the Nationa Research Corporation to its roster Sustaining Members.

This firm, with its main offices an the Research Division in Cambridge Massachusetts, and its Equipmen Division in Newton, Massachusetts is engaged in the development of proc esses in the fields of metallurgy, ino ganic and organic chemistry, applie physics, and coatings. The Equipmen Division is a major supplier of hig vacuum components and completel engineered installations. Such equip ment is usually employed in the chem ical, electronic, metallurgical, coatin distillation, food, and pharmaceutica industries. National Research employ 365 people.

Officers heading the company are Richard S. Morse, President; Robert A. Stauffer, Vice-President in Charg of Research; Harold C. Weingartne Vice-President and General Manager the Equipment Division; E. Norma Staub, Treasurer.

In the metallurgical field, Nationa Research Corporation was responsibl for the large-scale development of th Pidgeon Process for thermal reductio of magnesium and for its importan fundamental work in vacuum melting and coating such as is used in convertin titanium sponge to ingot. Significant among research activities are projects devoted to development of a low cos titanium reduction process, the applica tion of coatings for protecting metals a high temperatures, and the application of thin metallic films to metallic an nonmetallic substrates.

National Research is known for its development which led to the formation of its licensee, the Minute Maid Cor poration, and the introduction of froze citrus concentrates to the market.

General Motors Founds Electrochemistry Fellowship

The Department of Chemistry of the University of Michigan has announced the establishment of a graduate fellowship in Electrochemistry by General Motors Corporation, Detroit, Michigan. The fellowship carries a cash award amounting to $1800 to the fellowship holder and $1000 to the University to cover the cost of tuition, special apparatus, and other incidentals.

The fellowship will be offered first in 1952–53 and is subject to renewal for a period of one year. The research is to be of a fundamental nature suitable for a doctoral dissertation in the field of Electrochemistry. The recipient will be nominated by the teachers of Electrochemistry of the Department of Chemistry.

Society Cites Industrial Needs

For several years, it has been realized by The Electrochemical Society and the electrochemical industries that there is a marked deficiency of properly trained electrochemists. To make a thorough study of this situation, a standing committee of The Electrochemical Society was appointed in the spring of 1949. This committee is to consist of the President and the three Vice-Presidents each year. Results of various questionnaires sent to the heads of chemistry and chemical engineering departments in various academic institutions and to directors of electrochemical research in industry and in research institutes demonstrate the following:

1. There is a pronounced tendency for chemistry departments to eliminate electrochemistry from the curriculum. The reasons for this appear to be (*a*) failure of personnel interviewers to make known the need for electrochemists in their own company; (*b*) lack of expressed interest on the part of students, which in turn has been due to lack of knowledge of opportunities in the electrochemical field; (*c*) decline in the number of qualified teachers of the subject, and (*d*) increasing demand in the curriculum for additional courses in the newer and more glamorous phases of physical chemistry.

2. Industries and research organizations employing electrochemists have failed to make known to academic institutions the rapid expansion of the field and the consequent demand for trained men. The reason cited for this is that for many years, when men trained in electrochemistry were requested from chemistry departments, no such men were available. This led to adoption of the plan of training the man on the job, which is admitted to be highly expensive and unsatisfactory.

Both of these situations have resulted in lack of knowledge on the part of students of the fact that there actually do exist great opportunities in this rapidly expanding and diversified industry.

When this information was brought to the attention of the Personnel Department of the General Motors Corporation, their cooperation was immediate and enthusiastic, and soon resulted in the establishment of the above-mentioned fellowship as their contribution to the correction of an unfortunate situation.

Applicants for the fellowship should write at the earliest possible date to Professor Alfred L. Ferguson, Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

Further information on the current demand for electrochemists is given in a recent article on "Modern Industries Depend on Electroprocesses" by Charles L. Faust of Battelle Memorial Institute, which shows the magnitude of this field. A reprint may be obtained on request from Professor Ferguson.

Triple Superphosphate Plant for Davison

The Davison Chemical Corporation of Baltimore has started construction of a plant for the production of triple superphosphate at Ridgewood, near Lakeland, Florida.

Davison, now producing phosphate rock and normal superphosphate, as well as mixed fertilizers and general industrial chemicals, will for the first time become a producer of triple superphosphate when the new plant is completed. Expected date—October 1, 1953.

DIVISION NEWS

Electrothermic Division

J. S. Dewar, National Carbon Limited, Toronto, has been appointed Program Chairman for the Electrothermic Division of the Society for the 1952 fall meeting in Montreal, and for the 1953 spring meeting in New York City.

Mr. Dewar will be pleased to hear from anyone who has any ideas or suggestions, particularly for the New York Meeting, or who is interested in helping to plan the program. They should communicate with him at 805 Davenport Road, Toronto 4, Canada.

C. H. CHAPPELL, *Chairman*

SECTION NEWS

Philadelphia Section

During the month of June the Philadelphia Section conducted a mail balloting for the election of Section officers for the 1952–53 term. The nominating committee, comprising Arthur Osol, chairman, H. S. Lukens, and R. H. Cherry, proposed as the slate of candidates the present officers of the Section.

As the result of an unusually good response from the members, the candidates were unanimously elected and, accordingly, the officers for the coming term are:

Chairman—John F. Gall
Vice-Chairman—J. Fred Hazel
Treasurer—George F. Temple
Secretary—Edgar L. Eckfeldt

E. L. ECKFELDT, *Secretary*

San Francisco Section

At the last meeting of the San Francisco Section for the 1951–52 season, held May 28, at the Faculty Club of the University of California, Berkeley, California, the following officers were elected to serve during the coming year:

Chairman—Richard F. Bechtold, The Dow Chemical Company, Pittsburg, California
Vice-Chairman—Charles W. Tobias, University of California, Berkeley, California
Secretary-Treasurer—Henry F. Myers, Columbia Steel Company, Pittsburg, California

The retiring Chairman of the Section, Dr. Edward B. Sanigar, U. S. Naval Radiological Defense Laboratory, San Francisco, was the guest speaker at the above meeting, delivering an address on "Electrophoresis."

RICHARD F. BECHTOLD, *Chairman*

India Section

Second Annual Meeting

The Proceedings of the second annual meeting of the India Section of the Society, held on June 27, in Bangalore, are outlined below:

The business meeting was held first, with Dr. B. K. Ram Prasad presiding.

After confirming the minutes of the previous meeting, Dr. T. L. Rama Char, Secretary-Treasurer, presented the second annual report (1951–52) covering the activities of the Section: meetings, Section and Society membership and dues, patrons of the Section, committees of the Society and the Section, JOURNAL of the Society and contribution of an article on "The Development of the Electrochemical Industry in India," the publication of the first two issues of the *Bulletin of the India Section of The Electrochemical Society*, and miscellaneous activities such as participation in symposia.

The Secretary concluded by stating that the Section had grown and its activities increased and he hoped that it would play a more useful part in the future. He then expressed his thanks to the President and Board of Directors of the Society, Dr. H. B. Linford, the Secretary, Dr. R. M. Burns, Chairman, Publication Committee of the JOURNAL of the Society, the Chairman and Officers of the Section, the members of the various committees, and the members and patrons of the Section, for their cooperation during the year.

The following members were elected as officers for 1952–53:

Chairman—M. S. Thacker

Vice-Chairmen—K. Rajagopal and Charat Ram

Secretary-Treasurer—J. Balachandra

Next, matters pertaining to 1953 were discussed. Professor M. S. Thacker and Dr. S. Krishnamurthy then spoke expressing the deep sense of appreciation of all for the services rendered by the retiring Chairman, Dr. B. K. Ram Prasad, and Secretary-Treasurer, Dr. T. L. Rama Char, ever since the formation of the Section. With a vote of thanks to the Chair, the meeting came to a close.

At the technical session, Dr. B. K. Ram Prasad delivered an address on "The Latest Developments of the Electrochemical-Metallurgical Industries in India, with special reference to the Bombay area." A vote of thanks was given to the speaker, proposed by Dr. T. L. Rama Char.

J. BALACHANDRA, *Secretary-Treasurer*

CHANGE OF ADDRESS

The Institute of Metal Finishing, incorporating Electrodepositors' Technical Society, has moved to new offices at 32, Great Ormond Street, Holborn, London, W.C.1.

Summary of Activities of India Section (1951–52)

A summary of the activities of the India Section for the past year follows:

Meetings.—There were 3 technical meetings and 2 business meetings of the Section, 1 meeting of the Executive Committee, and 8 meetings of the Bulletin Editorial Committee. The First Annual Meeting of the Section was held on August 2, 1951.

One of the technical meetings was held at Mettur; the program included visits to factories and places of interest in the Mettur area. The Section is thankful to the authorities of the Mettur Chemical & Industrial Corporation, Ltd., for giving all facilities in arranging for the meeting. It is hoped that it will be possible to hold at least one technical meeting each year at an electrochemical center outside Bangalore.

Members of the Section.—The number increased during the year from 28 at the end of 1951 to 36 to date. More will join from among those newly elected by the Society. Most of the members of the Society in India are members of the Section.

Enrollment of new members to the Society.—The Section handled membership applications. The number of members admitted to the Society through the Section was 14 (as against 8 during the previous period) and 2 applications have been sent to New York.

Membership Dues.—Section membership dues were fixed at Rs. 2-8-0. Society dues are collected and transmitted to New York. Most of the members are availing themselves of this facility.

Patrons of the Section.—There are now 9 patrons (as against 6 during the previous period); the patrons newly enrolled are: P.S.N.S. Ambalavama Chettier & Co., Ltd., Madras, The Mettur Chemical & Industrial Corporation Ltd., Mettur Dam, and The Engineering and Mineral Industrial Research Laboratory, Bangalore. The Section should put in more efforts to enroll new patrons. The patrons continued to be invited to technical meetings and furnished technical information when it was requested.

Committees.—The following members have served on various committees:

SOCIETY—(1) Membership Committee: B. K. Ram Prasad and V. M. Dokras. (2) Local Section Advisory Committee: Charat Ram and K. Rajagopal. (3) Journal-Regional Editor for India: T. L. Rama Char.

SECTION—(1) Executive Committee: B. K. Ram Prasad, J. Balachandra, K. Rajagopal, V. Aravamuthan, T. L. Rama Char. (2) *Bulletin* Editorial Committee: B. K. Ram Prasad, J. Balachandra, V. Aravamuthan, S. Krishnamurthy, T. L. Rama Char. (3) *Bulletin* Advisory Board: Charat Ram, K. L. Ramaswamy, V. M. Dokras, K. Seshadri, S. Ramaswamy, A. Joga Rao, B. Narayana Das, L. C. Jariwala. (4) Nominating Committee: V. Aravamuthan, A. Joga Rao, K. Seshadri. (5) Advisory Committee: V. Aravamuthan, S. Krishnamurthy.

Bulletin.—The Board of Directors of the Society approved of the proposal of the Section to issue a *Bulletin of the India Section of The Electrochemical Society*. An Editorial Committee and Advisory Board were appointed, and it was decided to publish a quarterly. Two numbers, namely January 1952 and April 1952, have been issued. It is distributed to members and patrons, the Society Journal and Local Sections, and important scientific institutions. Members will be glad to know that the *Bulletin* has been well received by the Society. The feasibility of getting it printed is being investigated.

The *Bulletin* will be one of the important activities and the Section should see that it maintains as high a standard as possible. Members are requested to extend their cooperation by furnishing, from time to time, any information available to them for publication.

Other Activities.—The Section is doing its best to stress the importance of electrochemical research, teaching, and industry. In response to an invitation from the National Metallurgical Laboratory, Jamshedpur, the Section participated in a symposium on "Electroplating and Metal Finishing" held in March 1952. Information on "The Teaching of Electrochemistry and Electrochemical Engineering" was sent to the Chairman in connection with the formulation of the course of studies in Electrochemical Technology by the Andhra University. The electrochemical and allied industries in India are taking interest in the activities of the Section by becoming patrons and sending advertisements for publication in the *Bulletin*. They are also asking for technical information in the electrochemical field. The Section is quite hopeful that there will be increasing cooperation between it and the industries.

J. BALACHANDRA, *Secretary-Treasurer*

PERSONALS

GEORGE KEELERIC, formerly associated with United Drill and Tool Corp., Chicago, is now connected with Super-Cut Inc., Chicago.

ROBERT M. PARKE is now at the General Electric Research Laboratory at the Knolls, Schenectady, New York. Mr. Parke had been at Battelle Memorial Institute, Columbus, Ohio.

DENNIS R. TURNER has joined the Chemical and Metallurgical Department of Bell Telephone Laboratories, Inc., Murray Hill, New Jersey. Dr. Turner was formerly with the Electroplating Projects Laboratory, Westinghouse Electric Corp., East Pittsburgh, Pa.

HYMAN CHESSIN has been appointed Assistant Professor and head of Chemistry Section, Arno Project, Institute of Science & Technology, University of Arkansas, Fayetteville, Ark. Dr. Chessin had been in the Department of Chemistry, Kenyon College, Ohio.

EDWARD F. FOLEY, JR., has joined the staff of Enthone, Inc., New Haven, Conn., as a research chemist. Mr. Foley was formerly Research Assistant in the Chemical Engineering Department, Columbia University.

SAMUEL COTTRELL has transferred from Mathieson Chemical Corp., Baltimore, Md., to the company's plant at Little Rock, Ark

M. K. T. REIKE has resigned as Director of Research for the Longhorn Tin Smelter, Texas City, Texas, to accept a position as metallurgical engineer with Singmaster & Breyer, Consulting Chemical Engineers and Metallurgists, New York City.

JOHN F. GALL has been appointed Director of the Inorganic Research Department, from Supervisor of Research, at Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.

JACK BAIN HEADS JOURNAL ADVERTISING

Jack Bain, Publishers Representative, 545 Fifth Avenue, New York City, has been appointed advertising representative for the JOURNAL of The Electrochemical Society, effective September 1.

Mr. Bain has wide experience in this field having operated a Publishers Representative organization in New York for the past 18 years, specializing in trade and technical publications. During 1941–45 he served as Business Manager and Advertising Manager for the American Electroplaters' Society, and was publisher for that Society's official organ, *Plating*.

He was responsible, in part, for organizing the Association of Publishers Representatives, and is serving this year as president. He is a graduate of Oberlin College.

Mr. Bain will be in charge of the advertising program of the JOURNAL and can be reached at his office, 545 Fifth Avenue, Suite 1109, New York, N. Y., (Murray Hill 2-3345) or through the JOURNAL office.

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Research and Development Laboratory
9036 Culver Blvd. Culver City, Calif.

DAVID A. PRITCHARD

David A. Pritchard, prominent in the electrochemical industries for many years, died at his home in Montreal last May.

Mr. Pritchard was born in Wales and came to the United States in 1910, where he was associated with the Pennsylvania Salt Manufacturing Company and the Du Pont Company. From 1915–22 he was in England, and resigned as electrochemical superintendent of Imperial Chemical Industries, Ltd., to come to Canada. He joined the Canadian Salt Company at Windsor, Ontario, and was instrumental in building a chlorine liquefaction plant, and in developing the triple salt process. From 1931 until his retirement in 1946, he was connected with Canadian Industries, Ltd.

Mr. Pritchard was long active in The Electrochemical Society which he joined in 1917; he was a member of the Board of Directors from 1930–33.

LETTER TO THE EDITOR

Deposition of Trace Elements

Dear Sir:

A recent paper[1] suggested that the reason the deposition behavior of certain trace elements, such as bismuth, followed the abbreviated Nernst Equation when deposited onto an inert metal electrode[2] was because few sites on the inert electrode offered a bond to the bismuth atom as strong as, or stronger than, that of a deposited bismuth atom. Hence, even if a very large inert electrode were used, one would expect the rate of deposition of bismuth at a particular potential to be proportional to the number of sites offering such bonds, providing the potential were such that bismuth would deposit readily upon a bismuth surface. One would expect to find the rate of deposition to be slow at the start and to increase with time as the fraction of the electrode area represented by bismuth increased. The rate should reach a maximum as soon as the electrode was completely covered with bismuth, following which the rate should fall off as the concentration of bismuth decreased during the electrolysis.

Exactly this behavior has recently

[1] J. T. BYRNE AND L. B. ROGERS, *J. Electrochem. Soc.*, **98**, 461 (1951).

[2] J. DANON AND M. HAISSINSKY, *J. Chim. Phys.*, **47**, 951 (1950).

been reported for the deposition of bismuth onto either a platinum or a copper electrode from a solution containing an initial concentration of 500 mg/l of bismuth in 0.25*M* tartrate and 0.10*M* chloride.[3] Although the composition of this solution does not duplicate those used by Haissinsky and his coworkers, it appears reasonable to conclude that qualitative confirmation of the explanation for such trace behavior has been obtained. Although Lingane and Jones do not report an overvoltage for bismuth in their polarographic studies with a platinum electrode, it is reasonable to expect that this overvoltage should be observed in the same way that undervoltages have been observed in similar polarographic (and deposition) studies with platinum electrodes of very dilute solutions of silver.[4] The fact that an overvoltage rather than an undervoltage has been observed many times for the initial polarogram of silver ion using a new graphite electrode indicates that traces of silver might, like bismuth, deposit according to the abbreviated Nernst Equation if graphite electrodes were substituted for platinum.

It is interesting to note that there are also evidences of similar overvoltage effects with mercury cathodes. In at least one case the polarographic half-wave potential with a dropping mercury electrode is about 0.1 volt more cathodic than that on a pool of stationary mercury in which the deposited element is allowed to accumulate.[5] It appears, therefore, that the deposition behavior of trace elements at a mercury cathode will be as complex as anticipated.[6]

L. B. Rogers
Massachusetts Institute of Technology,
Cambridge, Massachusetts

[3] J. J. Lingane and S. L. Jones, *Anal. Chem.*, **23**, 1801 (1951).

[4] H. H. Miller and L. B. Rogers, Unpublished results.

[5] T. L. Marple and L. B. Rogers, Unpublished results.

[6] L. B. Rogers, *J. Electrochem. Soc.*, **99**, 267 (1952).

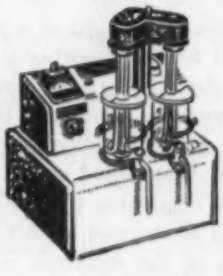
CORRECTION

In the August issue of the Journal on page 203C, column 1, the reaction should read:

$$Cu_2Cl_2 + Mg + 6H_2O \rightarrow 2Cu + MgCl_2 \cdot 6H_2O.$$

Eberbach *DYNA-CATH Is Fastest*

Mercury Cathode Apparatus



For determination of cerium in stainless steel, aluminum in steel, aluminum in zinc base alloys, and other separations—DYNA-CATH is a completely new high speed mercury cathode apparatus which accelerates and does a more complete job in the analytical separation of metals. For example, DYNA-CATH quantitatively removes 5 grams of iron from 100 ml of electrolyte in 60 minutes. It overcomes the difficulties which have prevented utilization of the mercury cathode as an analytical tool.

Write for Bulletin 220

Eberbach CORPORATION
SCIENTIFIC INSTRUMENTS & APPARATUS
ANN ARBOR, MICH.

BOOK REVIEWS

Gmelins Handbuch der Organischen Chemie. System No. 27 Magnesium Teila-Lieferung 4, Legierungen v Magnesium mit Zink bis Rhenium Oberflachenbehandlung. Published Verlag Chemie, GMBH, Weinheim Bergstrasse, 1952.

With this issue the publishers ha completed their study of magnesium It comprises pages 483 to 818 of t study and cites literature publish through the end of December 19 Subjects covered include the chemic physical, and mechanical properti of magnesium alloys with Zn, Cd, H In, Tl, Re, Ti, Zr, Th, Ge, Sn, P Mn, Ni, Co, Fe, Cu, Ag, Au, as well some other elements on which lit information is presented. Many terna systems are also described as well as few higher polynary systems. Th section of the book comprises pag 483 to 750. The surface finishing magnesium for protection against co rosion is summarized on pages 760 817.

To complete the descriptive pictur of the coverage of this handbook magnesium, the first part, pages 1 156, covered the literature to Apr 1937 and summarized the history magnesium, its extraction, and co mercial processes for its fabrication. Th second part covered the literature May 1937 and summarized data on th physical properties, chemical and ele trochemical properties, as well as analyt ical methods. The third part of th handbook covered the literature to Ma 1942 and described alloys of magnesium and Si, Sb, Li, Na, K, In, Ca, Ar, an Ba, as well as brief mention of a fe other alloying elements.

The present and final issue of the mag nesium portion of the handbook co tains an extensive and exhaustive cita tion of original literature bearing on th subjects discussed. Much of this litera ture is summarized factually.

The graphs and tables from the mor important articles are presented. Th literature does not appear to have bee examined critically. That is, discrepan cies in results of different investigator are not discussed nor is any attempt made to determine which references may b the most authoritative.

It is unfortunate that the most im portant alloying system, magnesium-aluminum, is not covered in this book Reference only is made to the alumi num section of the handbook for mag

sium-aluminum alloys. The coverage of alloys is really thorough as exemplified, for example, by the 37 pages on magnesium-zinc and 30 pages on magnesium-silver.

The book is an indispensable work of reference for research workers in the field of magnesium.

JOHN C. MCDONALD

THERMODYNAMICS OF ALLOYS by Carl Wagner. Published by Addison-Wesley Press, Inc., Cambridge, Mass., 1952. viii plus 161 pages, $6.50.

Enlarged and revised translation of the treatise "Thermodynamik metallischer Mehrstoffsysteme" from *Handbuch der Metallphysik*, Volume 1, Part 2, edited by G. Masing (Akademische Verlagsgesellschaft Becker and Erler Kom.-Ges., Leipzig, 1940). Translated by Mellgren and Westbrook.

This treatise was translated in 1948. The present volume is the original author's enlargement and revision of that translation. The new material is substantial and includes presentation of new methods and data as published between 1940 and 1951, together with "new sections on ternary and high-order component systems, empirical formulas, and relations between thermodynamic functions and the electronic constitution of alloys."

Within the short span of only seven chapters, the author presents a remarkably detailed picture of the current status of the whole of this important subject. The pace is rapid and all excess verbiage is avoided. Deficiencies in current theory or data are clearly noted.

Chapter 1 introduces the thermodynamic relations that are to be used and presents clear and forthright definitions of all important terms and concepts. This theoretical material is then applied in Chapters 2, 3, and 4, respectively, to problems associated with disordered solutions—both liquid and solid—ordered solutions, and to relations between thermodynamic functions and the phase diagram. Chapters 5, 6, and 7 then present and discuss experimental methods and results that relate to these problems—in particular, heats of formation, activities, and equilibria in liquid alloys and melts of salts.

The bibliography is uncommonly complete, containing 419 entries. In addition to the usual Subject Index, there is an Alloy Index which greatly enhances the reference value of the volume.

J. N. HOBSTETTER

RECENT PATENTS

Selected for electrochemists by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

June 17, 1952

Friedman, M., 2,600,526, Rechargeable Dry Cell Battery

Shockley, R. E., 2,600,699, Zinc-Copper-Tin Alloy Plating

Castlen, R. C., 2,600,732, Indicator-Type Adapter for Battery Cell Caps

Zaccagnini, C. L., 2,600,823, Hot Top Electrode Tip

Lark-Horovitz, K., and Whaley, R. M., 2,600,997, Alloys and Rectifiers Made Thereof

Wolfe, J. K., 2,601,014, Preparation of Fluorinated Chlorocarbon Compounds

Jacobs, H., and Hees, G., 2,601,024, Electrode Structure for Electron Discharge Devices

Larach, S., 2,601,032, Manganese Activated Zinc Barium Silicate Phosphor

Masterton, J., 2,601,043, Protective Means for Electricity Storage Battery Cases

Yardeny, M. N., 2,601,133, Rechargeable Battery

Spencer, P. L., 2,601,178, Method for Producing Fluorescent Screens

Fritzlen, T. L., 2,601,206, Medium-Strength Corrosion-Resistant Aluminum Alloys

Robinson, H. A., 2,601,214, Cathodic Protection of Underground Metals

June 24, 1952

De Ment, J., Application 748,632, Method and Means for Protection of Ships and Buildings from Radioactive Weapons

De Ment, J., Application 791,074 Method and Means for Structure Surface Protection

Ellis, G. B., 2,601,267, Primary Alkaline Cell

Fastie, W. G., 2,601,508, Compensated Thermopile

Lancy, L. E., 2,601,535, Electrolytic Treating Apparatus

July 1, 1952

Calvin, M., and Weigl, J. W., 2,602,047, Method of Concentrating Isotopic Carbon

Faus, H. T., 2,602,095, Thermoelectric Device

(Continued on page 290C)

New METALLURGY BOOKS

METALLURGICAL ENGINEERING

By Reinhardt Schuhmann, Jr.
Massachusetts Institute of Technology

390 pp, 155 illus, 1952, $7.50

Presents metallurgical engineering according to basic principles and unit processes rather than according to metals treated. Stresses integration of physical chemistry with metallurgical engineering and emphasizes analysis and quantitative solution of engineering problems rather than descriptive treatment of current practices.

THERMODYNAMICS OF ALLOYS

By Carl Wagner
Massachusetts Institute of Technology

161 pp, 37 illus, 1952, $6.50

Summarizes principles of thermodynamics of binary and multicomponent systems; methods of experimental determination of characteristic thermodynamic quantities such as heat of mixing formation, partial free energies of mixing, activities, etc.; methods of calculating thermodynamic quantities from other quantities which have been measured; available experimental data and indirectly obtained values; atomic and electronic interpretation of data; treatment of equilibria between alloys, salt melts, oxide melts, silicate melts, etc.

ELEMENTS OF CERAMICS

By F. H. Norton
Massachusetts Institute of Technology

246 pp, 194 illus, 1952, $6.50

Presents principles underlying the various processes used in the ceramic field with illustrative applications. Emphasis is on unit processes rather than products. A complete reference for research workers and ceramic engineers, by one of the foremost authorities of the present time.

ELEMENTS OF PHYSICAL METALLURGY

By A. G. Guy, *Purdue University*

293 pp, 218 illus, 1951, $6.50

Fundamentals of physical metallurgy with emphasis on underlying ideas of the subject rather than applications. Important applications are introduced as illustrative examples. Examples are made quantitative rather than merely qualitative. A broad, unspecialized coverage of the whole field, including an unusual appendix of the literature of metallurgy.

The above books are part of

THE ADDISON-WESLEY METALLURGY SERIES

Morris Cohen, *Consulting Editor*

Detailed descriptions of above books are available upon request

ADDISON-WESLEY PRESS, INC.
CAMBRIDGE 42, MASS

Welch, C. H., and Welch, J. M., 2,602,-105, Battery Terminal Connection.

July 8, 1952

Hunrath, G., Application 194,005, Method of Improving Electrolyte Paste

Scaff, J. H., and Theuerer, H. C. 2,-602,211, Rectifier and Method of Making It

Binder, W. O., and Thompson, J., 2,602,737, Corrosion Resisting Steels

Jennings, P. A., 2,602,738, High-Temperature Steel

Scaff, J. H., and Theuerer, H. C., 2,-602,763, Preparation of Semiconductive Materials for Translating Devices

Beaver, J. F., 2,602,774, Method of Plating Copper

Isherwood, E. I., 2,602,775, Electrodeposition of Zinc

Mould, G. J. J., 2,602,776, Electrolytic Method of Winning Zinc

Stumbock, M. J., 2,602,826, Process for Manufacturing Alkaline Storage Batteries

Brennan, J. B., 2,602,843, Electrolytic Cell

Fraenckel, V. H., and Koller, L. R., 2,-602,900, Luminescent Screen

July 15, 1952

Blickensderfer, P. S., 2,603,593, Electrodeposition of Metals

Woodman, F. W., and Crowell, J. M., 2,603,594, Method of Electrolytically Producing Manganese

Reydel, G. H., 2,603,595, Plating Thickness Meter

Vangsnes, K. T., 2,603,596, Anode Suspension and Electrical Connection

Chappell, C. H., 2,603,669, Large Electrode with Thermal Stress Relief

Pahler, C. F., 2,603,670, Storage Battery

Burns, H. C., and Wilson, H. D., 2,-603,671, Battery Assembly

Reppert, R., 2,603,672, Cover Construction for Storage Battery Cells

July 22, 1952

Cushing, R. E., 2,604,441, Method of Producing Inorganic Compounds of Increased Oxidation State

Lambert, J. M., and Hamm, F. A., 2,604,442, Production of Metal Powders of Small Size

July 29, 1952

Schaefer, R. A., and Mohler, J. B., 2,605,149, Bearing

Freud, H. M., dit Frasch, Jean, 2,605,-217, Protection of Metallic Objects by Galvanic Action

LITERATURE FROM INDUSTRY

COLLOIDAL GRAPHITE. Six-page, two-color bulletin on "Colloidal Graphite for Surface Coatings and Impregnation." Electric furnace graphite of high purity, when rendered colloidal and dispersed in a suitable carrier, finds new uses as a dry-film lubricant—surface coating for many mechanical devices—and as an impregnating medium for such materials as porous minerals, cloth, asbestos, etc. Acheson Colloids Co. P-64

DIMENSIONAL DATA SHEETS on a line of valves for fluid control have just been released. These sheets give complete valve dimensions which should prove extremely valuable in planning or designing new equipment in instrumentation or industrial fields. Hoke, Inc. P-65

VOLTAGE REGULATED POWER SUPPLIES. 20-page catalogue and new condensed brochure have just been released describing voltage regulated power supplies; of interest to all users of electrical and electronic equipment. Kepco Laboratories, Inc. P-66

PLASTIC COATING FOR SPRAY BOOTHS. Two-color leaflet describes the use and application of a new vinyl-type coating for paint spray booths. The coating is easily peeled off, taking with it all paint overspray, to give quick, low-cost maintenance. Detrex Corp. P-67

GAGES AND VALVES. New folder describes line of liquid level gages and valves, water columns, gage illuminators, etc. Jerguson Gage & Valve Co. P-68

VIBRATION METER. New 4-page bulletin describes the 1-110B Vibration Meter, a simple and compact instrument, which gives *direct* readings of both linear and torsional velocity and displacement, allowing rapid, easy calculation of the vibrational characteristics of machines and structures. Consolidated Engineering Corp. P-69

PUMP APPLICATION GUIDE. A new type of reference chart on small pump applications lists the various types pumps, services for which each is b performance, and special features each. Tuthill Pump Co. P

DIFFERENTIAL-VOLTAGE INDICAT Bulletin describes a new indicator, signed to measure differential volt as well as amperage, speed, pressure, other quantities which can be conver to voltage. Features a self-balanc circuit with a high degree of stabil and freedom from drift; can be set indicate full scale for voltages as sm as 0.022 volts, and can be used w standard accessories, etc. General El tric Co. P

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

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EMPLOYMENT SITUATIONS

Please address replies to box show % The Electrochemical Society, In 235 W. 102nd St., New York 25, N.

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RESEARCH ASSOCIATE of Americ Electroplaters' Society to work National Bureau of Standards on pe meability and protective value of el troplated coatings. College graduat Salary $3400–4200 per year. Applic tion should include qualifications a minimum acceptable salary. Reply *Box A-242.*

Positions Wanted

CHEMICAL ENGINEER, B.S., 193 M.S. 1952, 6 years' industrial plus years' Civil Service experience in el trochemical field (plating, batteries supervision, development, researc Adaptable, mechanically inclined. Avai able September. *Reply to Box 349.*

ELECTROCHEMIST, Ph.D., industri experience in deposition, corrosio analytical instrumentation. Present sa ary $6500. Desires position in industry Available in 15–30 days. *Reply to Bo 350.*

Editorial

Industrial Electrolysis

THE Industrial Electrolytic Division is happy to join in celebrating the Fiftieth Anniversary of The Electrochemical Society. A few of the industries represented in the Division are older than the Society but most are younger. The Industrial Electrolytic Division was organized to serve the interests of those electrochemists manufacturing chemicals and winning metals by the electrolytic method. Fifty years ago, salt was already being electrolyzed to make caustic soda and chlorine by both the mercury cell and diaphragm cell process. Sodium chlorate was also being made. Hall had developed his process for aluminum, and sodium was being made by electrolyzing fused sodium hydroxide. This list of products has grown during the life of the Society with sodium perchlorate and hydrogen peroxide among the chemicals. Electrolytic sodium hypochlorite has occasionally been made. Sodium is now made from fused salt rather than fused caustic soda. Other metals obtained electrolytically include beryllium, bismuth, calcium, cadmium, cerium, chromium, cobalt, copper, gold, indium, lead, lithium, magnesium, manganese, nickel, silver, tin, uranium, and zinc. Will titanium and some of the "rare" metals join the group?

Members of the Division have prepared eight review articles covering various fields. The aluminum industry is covered historically and, in addition, recent technical advances in Europe are brought to our attention. The biography of an early but little known experimenter in aluminum, Augustus J. Rogers, is given in the Feature Section. The magnesium and sodium industries were reviewed individually while other metals were reviewed as a group. Reviews were obtained on alkali-chlorine, chlorates and perchlorates, and hydrogen peroxide. The Division is indebted to the individual authors.

Several of these industries were operated almost as secret processes for many years. The great expansion during World War II required the licensing of many

(*Continued on next page*)

Editorial (*continued*)

processes and passing on of "know-how" to licensees. The technology became so widely known that publication policies became more liberal. German processes were investigated after the war and details published so that a great deal of information is now generally available. The Division has been able to arrange symposia on a number of subjects of mutual interest.

One of the common interests of those in the Industrial Electrolytic Division is cheap direct current. Power is one of the major costs in most of these industries. Motor generators and synchronous converters served the industry for many years. Conversion efficiencies were of the order of 80 and 90 per cent, respectively, depending on the circuit voltage. Cell circuits were built up with a number of cells in series to arrive at the efficient operating voltage and the desired production capacity. The mercury arc rectifier was developed in the thirties and improved efficiencies were obtainable, if circuit voltage of 500 to 700 volts could be used. Practically all of the electrolytic expansion during World War II was with the ignitron type of mercury arc rectifier. This required special safety precautions because of the high voltage. At the end of the war, it was found that the Germans had been developing a mechanical rectifier of even higher efficiency. The high efficiency extends from 50 to a top-operating voltage of about 400 volts. Machines of advanced design are now being built in the United States and several high-amperage installations have been in successful operation for several years. High efficiency without the hazards of high voltage seems like the answer to the industrial electrochemist's prayer.

Another trend in electrochemical circuits has been toward larger and larger cells. Electrolytic cells require a considerable amount of individual control and maintenance. A large cell can be controlled as readily as a smaller one so labor costs can be reduced by increasing cell size. The largest units are in the aluminum industry where one hears of 100,000 ampere "pots." Magnesium cells have been operated at 75,000 amperes and mercury type caustic-chlorine cells are operating at 50,000 amperes. Cells of such a size can't equal the daily production of a blast furnace but they are working in the right direction.

—William Cecil Gardiner

Fiftieth Anniversary

INDUSTRIAL ELECTROLYSIS

Fifty Years' Progress in Electrowinning and Electrorefining

A. C. Loonam[1]

In 1902, when The Electrochemical Society was founded, the word "electrometallurgy" was synonymous with electroplating to a great many people and at least one book on plating with that title was in circulation. However, what may be termed the "electrolytic metallurgical industry" was in a state of great activity. Faraday's laws had been known for more than sixty years; Lorenz had found that they apply to fused salts as well as aqueous solutions; Davy, Bunsen, and others had shown that practically any metal could be recovered electrolytically under the proper conditions; and large supplies of power were available from newly installed steam and hydroelectric plants. Indeed, the time might well be termed a period of overoptimism as there were many who thought that electrochemistry was the key to the solution of all metallurgical problems. It is not surprising, therefore, that men like Hoepfner, Borchers, Ashcroft, and engineers of Siemens and Halske were busy devising processes for the extraction and recovery of all of the then common metals and that patents were being issued at high rates in the major industrial countries. Some of these processes reached pilot plant and even industrial scales of operation before they were abandoned, and many very valuable details were disclosed which were later incorporated in other and more successful processes.

Furthermore, the industry had reached a position of considerable commercial importance. The Hall-Heroult process was 14 years old and had produced 7450 long tons of aluminum in 1901; the Castner sodium process was in operation at Niagara Falls, in England, and on the Continent; and electrolytic magnesium had already made its start in Germany. The histories of these metals are discussed in other articles.

Among the heavier nonferrous metals, the electrolytic refining of copper was well established. Ulke (1) listed ten refineries operating in the United States in 1902 with an annual total capacity of 339,450 short tons, and 23 in Europe with a capacity of about 46,000 short tons. It is of interest to note that, even at that time, eight of the American plants and 19 of the others used the "multiple" electrode arrangement, and that six of the American plants are still in operation. The Hoepfner electrolytic zinc process using a chloride electrolyte was operating in a plant at Winnington, England, which produced 1663 long tons of metal in 1901, and in two other plants on the Continent. The Moebius and the Balbach-Thum processes were in use for the parting of gold and silver, and gold was being refined commercially by the Wohlwill process.

The fifty years since 1902 have been a period of great expansion for the industry. Some processes are still in use on a larger scale, and new ones have been born and attained great importance. Considering the individual processes, the refining of copper has kept pace with the demand for that metal. There are now nine refineries in the United States with a total capacity of 1,700,000 short tons a year. The latest, that of the Kennecott Copper Corporation at Garfield, Utah, went into operation in June 1950, and has a capacity of 144,000 tons a year and can be readily expanded to 192,000 tons (2). The electrolyte contains 40 g/l Cu and 200 g/l H_2SO_4, current density is 16 amp/ft^2, and the cathodes are melted in electric furnaces.

The expansion of the industry has not been confined to the United States (3). Large modern refineries have been built in recent years in Canada, Germany, Sweden, Finland, Russia, Northern Rhodesia (4), Australia, and other countries. The two Canadian plants at Copper Cliff, Ontario, and Montreal East, Quebec, have a total capacity of over 230,000 tons a year. The Northern Rhodesian plant is unusual in that it was built to eliminate bismuth from the copper, which does not contain sufficient precious metals to pay for its refining.

Electrolytic refining has also become important in the treatment of secondary copper. Nearly 200,000 tons were recovered in the United States by this method in 1949. Most of this probably came from scrap treated at the primary refineries, but there is at least one electrolytic refinery in the United States operating exclusively on secondary metal.

The process is still basically the same as it was fifty years ago, but improvements have increased its efficiency and reduced costs. Adoption of a high acid electrolyte in the early 1920's reduced the cell voltage and therefore the power consumption (5), while direct casting of anodes at the smelter eliminated a melting and recasting operation.

Electrowinning of copper was not practiced in 1902, although the basic principles were known. The first large installation of this type was at Chuquicamata, Chile, to treat the oxidized ores of the huge copper deposit at that point. The process was worked out in a pilot plant at Perth Amboy, New Jersey, and operation of the full-scale plant started in 1915 (6). The ore is leached by percolation in large vats with spent electrolyte containing free H_2SO_4. The strong solution is treated to remove Cl as CuCl by treatment with "cement" copper, and electrolyzed in cells with insoluble anodes and copper cathodes (7). Because of nitrates and chlorides in the ore, it was originally planned to use magnetite anodes, but importation from Germany was stopped by World War I and Duriron anodes were substituted. These were later replaced by the "Chilex" copper silicide anode and ultimately by antimonial lead as the nitrate content of the ore decreased with depth.

Expanded several times, this plant reached a peak output of 243,565 tons in 1947, a figure exceeded among electrowinning plants only by the aluminum plant at Arvida, Quebec.

Subsequently, similar plants were built to treat oxidized copper ores at Ajo and Inspiration, Arizona, Potrerillos, Chile, and at Jadotville-Shituru in the Belgian Congo (8). The Ajo plant used SO_2 in solution as an anodic depolarizer; Inspiration maintains a concentration of ferric iron in the

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electrolyte which increases the solvent action on the sulfides in the ore, but does not seriously reduce current efficiency even in the absence of a diaphragm; Potrerillos used a solution purification similar to that used in zinc plants prior to electrolysis; and the Jadotville plant leaches by agitation.

This process may have seen its best days. The Ajo plant was shut down in the mid 1920's because of exhaustion of the oxidized ores, that at Potrerillos was shut down recently for the same reason, while at Chuquicamata a flotation plant and a smelter are being installed to take over as the oxidized ores become depleted. On the other hand, Inspiration produced 39,125 tons of copper in 1951, and the Jadotville-Shituru plant is being expanded to a total capacity of 100,000 tons a year.

It is generally supposed that electrolytic zinc from sulfate solutions is a product of World War I, but experiments were under way at Bully Hill, California, and at Trail, British Columbia, before that war broke out (9). The stimulus was probably the treatment of complex lead-zinc ores, since selective flotation was practically an unknown art at the time; but there is no question but that the demand of the Allies for high grade zinc for cartridge brass accelerated development of the process which went into commercial operation in a 100-ton a day plant at Great Falls, Montana, and a 60-ton plant at Trail about the year 1916.

The end of the war caused a sharp reduction in the demand for high grade metal and it became necessary at times actually to add impurities to the electrolytic product and sell it as Prime Western grade to avoid loss of the premium on the purer product. However, the development of zinc-base die casting alloys by the New Jersey Zinc Company and their adoption by the automobile industry soon supplied the needed markets for high grade metal.

The subsequent expansion of the industry was rapid. It now accounts for about 45 per cent of the world production of primary slab zinc, including all of that of Canada, Australia, Norway, and Northern Rhodesia, and 40 per cent of that of the United States. There are now at least 26 plants in the world with a total capacity of about 1,100,000 short tons a year (10). They are distributed among 13 countries and there is at least one on every continent. The latest plant to go into operation, that of the Cerro de Pasco Corporation in Peru, was expected to reach its rated capacity of 35 tons a day in the second quarter of this year.

There are five plants in the United States with a total of 3370 cells as of December 31, 1949 and a combined capacity of 938 tons a day. The newest is that of the American Smelting and Refining Company at Corpus Christi, Texas (11), with a capacity of 82 tons a day, which is soon to be increased to about 150 tons to treat zinc oxide fume from lead blast furnace slags. The current density is 60 amp/ft^2; the anode is the Tainton silver-lead alloy; and all of the product is Special High Grade, 99.99 per cent Zn.

Canada has two plants, at Trail, British Columbia, and Flin Flon, Manitoba, with a combined capacity of 600 tons a day. In December 1950, the Consolidated Mining and Smelting Company announced plans to increase the capacity of the Trail plant by about 70 tons a day.

The process remains basically the same as it was at the start, but there have been significant improvements in detail. Flash roasting, improved leaching cycles, more effective solution purification, the Tainton silver-lead anode, the mercury arc rectifier, and casting wheels have offset rising costs to some extent and have led to the production of higher purity metal. A large proportion of the output is now Special High Grade.

In the early 1920's, U. C. Tainton developed a modifie process, using a current density of 100 amp/ft^2 and a strong acid electrolyte operating at a high temperature, which wa installed in 1928 at the plant of the Sullivan Mining Com pany at Kellogg, Idaho, where it is still in operation. Subse quently, a second plant was built at East St. Louis for th Evans-Wallower Zinc Company (12), but was later shu down; and when it was taken over and rehabilitated by th American Zinc Company about ten years ago, the more orth dox current density of 30 amp/ft^2 was adopted.

To date, the electrolytic zinc process has stood up we against competition. The New Jersey Zinc Company's con tinuous vertical retort-fractional distillation process, and th St. Joseph Lead Company's electrothermic process, both which can produce high grade metal, have not seriousl affected its growth. The new Sterling electrothermic proces recently announced by the New Jersey Zinc Company, ma provide stronger competition as the Cerro de Pasco Corpor tion has postponed expansion of its electrolytic plant pendin the results of an investigation of this process.

An interesting application of electrolytic zinc developed i the 1930's is the Tainton or "Bethanizing" process for ele trogalvanizing of steel wire at the Sparrows Point, Maryland plant of the Bethlehem Steel Company. Leaching of roaste zinc concentrates with spent sulfate electrolyte and purifica tion of solutions are carried out as usual, but the cathodes i the electrolytic cells are moving steel wires upon which th zinc is deposited. The product is considered superior to wir produced by the hot-dip process.

Just about the time The Electrochemical Society wa founded, an electrolytic process for the refining of lead, de veloped by Anson G. Betts and using a solution of lead fluo silicate as the electrolyte, was built at Trail, British Columbia (13). Subsequently, plants were built at Omaha, Nebraska East Chicago, Indiana, and in other parts of the world. Th chief value of this process is its ability to remove bismuth The development of the Betterton process for the removal o bismuth by addition of calcium and magnesium to molte lead led to the closing of the Omaha plant, but those at Trail and East Chicago, with capacities of 170,000 and 42,000 ton a year, respectively, are still in operation. The latest plant at Oroya, Peru, had a capacity of about 44,000 tons a yea in 1945, but plans for expansion by converting part of a cop per refinery were announced in 1951. The electrolyte contain 80 grams of lead and 74 grams of free fluosilicic acid per liter the current density is 17.7 amp/ft^2, and the cell voltage 0.4 to 0.6 (14). A recent paper (15) describes a refinery nea Milan, Italy, with a capacity of 18 tons a day which uses a solution of lead sulfamate as the electrolyte.

The major proportion of the Canadian nickel output i refined electrolytically at two plants located at Port Col borne, Ontario, and at Kristiansand, Norway. Both us diaphragm cells from which the anolyte is withdrawn, treated to remove copper and iron, and returned to the cathode com partments. The Port Colborne process is relatively simple as the major separation of copper and nickel is accomplished during concentrating and smelting at Copper Cliff, but, a Kristiansand, electrolysis is a major step in the separate re covery of copper and nickel from matte by a modified Hyb nette process. Electrolytic copper is also produced at thi plant.

The Port Colborne plant has recently changed over from a sulfate to a sulfate-chloride electrolyte to secure increased conductivity and lower cell voltage or greater capacity. It would be of interest to find out whether the new method o

separation of copper and nickel now in operation at Copper Cliff has had any effect on the operation of this refinery.

The new hydrometallurgical process recently announced by the Chemical Construction Company (16) for the recovery of copper, nickel, and cobalt from complex ores may provide severe competition for electrolytic methods. It is now being installed in three plants which otherwise might have used the other.

Cadmium is a relatively valuable by-product of many lead and zinc plants. It is recovered from flue dusts or from the zinc dust precipitate in electrolytic zinc plants by wet methods, the final step of which is precipitation of the cadmium as a sponge on zinc slabs. In general, this sponge is refined in the pyrometallurgical plants by briquetting and distillation, and in the electrolytic zinc plants by dissolving in acid zinc cadmium sulfate solution, followed by electrolysis with lead anodes and aluminum cathodes. At Corpus Christi, Texas (11), the strong and spent electrolytes contain 200 and 100 grams of cadmium per liter, respectively; the current density is 10 amp/ft², and the cell voltage about 2.5. Probably between 40 and 50 per cent of the 11,000,000 lb produced annually in the world is recovered by electrolytic methods.

One of the most interesting developments of recent years, scientifically and practically, is the production of electrolytic manganese. This metal is considerably more electropositive than zinc; its deposition from aqueous solutions at commercial current efficiencies is therefore a real achievement. Furthermore, since there is no other commercial method for preparing high-purity manganese, the process makes available to industry what is practically a new metal.

Worked out on a laboratory and pilot plant scale in the early 1930's by Shelton and his coworkers at the U. S. Bureau of Mines, the process was brought to full scale by the Electro Manganese Corporation at its plant at Knoxville, Tennessee, which began operation in 1939, and, after several expansions, now has a capacity of 3600 short tons a year.

The process is similar to electrolytic zinc but with important differences (17). Since manganese occurs in nature chiefly as the higher oxides, the ores or concentrates must first be reduced to the strongly basic MnO prior to leaching. The electrolyte is a solution of manganous and ammonium sulfates. Solution purification is even more stringent than with zinc. Electrolysis is carried out in diaphragm cells using lead anodes containing small amounts of cobalt, antimony, and tin and stainless steel cathodes from which the manganese, which deposits in the brittle alpha modification, is broken off by flexing and hammering. The product is better than 99.9 per cent pure. Cell voltage is 5.0 to 5.3, cathode current density 40 to 50 amp/ft², and current efficiency 60 to 65 per cent. With the lead alloy anodes, only 2.5 per cent of the manganese fed to the plant is oxidized to MnO_2.

It was announced early in 1952 that the capacity of the Knoxville plant is to be doubled to 7200 tons a year and that the Electro Metallurgical Company will build a plant at Marietta, Ohio, with a capacity of 6,000 tons a year.

Electrolytic cobalt is produced at the rate of 200 to 300 tons per month at the Jadotville-Shituru plant of the Union Miniere du Haut Katanga in the Belgian Congo as a co-product in the electrowinning of copper (18). The cobalt builds up to about 6 to 7 g/l in the circulating leach-electrolyte, from which it is recovered as fairly pure cobalt hydroxide by a combination of lime precipitation, electrolysis, and cementation on metallic cobalt. The cobalt electrolyte contains about 100 g/l of cobalt hydroxide in suspension to keep it neutral. The principal impurity in the cathode cobalt is 3 to 5 per cent zinc, which is volatilized when the metal is melted in electric furnaces.

It is probable that there are other plants producing electrolytic cobalt. The Falconbridge Nikkelverk was expected to begin production from Canadian copper-nickel matte at its Kristiansand, Norway, refinery in 1951, and the United States Economic Cooperation Administration made a grant of $550,000 in 1950 to the Rhokana Corporation for a plant to produce it from a Northern Rhodesian concentrate (19).

It has been known for many years that metallic chromium can be deposited from chromic acid solutions containing small amounts of chromic salts. This process has been applied on a laboratory scale to produce small quantities of metallic chromium and has also been widely adopted for electroplating of this metal. However, this type of bath is not suitable for electrowinning or electrorefining as power yields are low because the chromium is deposited from the hexavalent state, current efficiency is low, and cell voltage is high. In the last five years or so, however, the U. S. Bureau of Mines has shown that chromium can be deposited from the trivalent state at current efficiencies well over 60 per cent (20). A diaphragm cell is used, current density is 80 amp/ft², cell voltage 4.8, and the catholyte is a solution of chromous, chromic, and ammonium sulfates. It was reported late in 1950 that the Electro Metallurgical Company planned to study a modification of this process, presumably for treatment of ferrochrome at its Marietta, Ohio, plant.

During World War I, the increased demand for tin and a shortage of Straits metal due to lack of shipping induced the American Smelting and Refining Company to construct and operate a smelter for Bolivian concentrates at Perth Amboy, New Jersey. The final step in the process was electrolytic refining (21). At first a stannous fluosilicate electrolyte was used, but this was later replaced by a sulfate-aromatic sulfonate solution. The plant reached a capacity of 1500 short tons a month, but was shut down a few years after the war when the supply of Straits tin again became normal.

Electrolytic parting of gold and silver in Dore bullion continues to expand. The tendency in recent years has been to favor the Moebius process, which uses vertical electrodes and sheet silver cathodes over the Balbach-Thum process with its horizontal electrodes and graphite cathodes placed at the bottom of the cells. Both use a weak solution of silver nitrate acidified with nitric acid as the electrolyte and enclose the anodes in cloth bags to catch the slimes which contain the gold and any platinum metals. In a modification of the Moebius process used by the Cerro de Pasco Corporation (14), the electrolyte is an almost neutral solution of silver and cupric nitrates, current density is 12 amp/ft², and the aluminum cathodes are stripped every 48 hours.

The Wohlwill process for refining of gold is also in a healthy state. An improvement introduced about 1910, the superimposition of an alternating current on the direct current, minimizes the tendency of silver chloride to form an impervious film on the anode. At the plant of the International Nickel Company (22), Copper Cliff, Ontario, the electrolyte contains 90–100 g/l gold and 100 g/l free hydrochloric acid, current density is 100 amp/ft², and the cell voltage 2.0. Apparently no alternating current is used, presumably because the impure gold, recovered from the slimes of Balbach-Thum cells, does not contain enough silver to require it.

Among the minor metals, bismuth was being refined electrolytically in Balbach-Thum cells using a $BiCl_3$-HCl electrolyte at the Omaha, Nebraska, refinery of the American Smelting and Refining Company in 1927, but it is not known whether the process in still in operation.

Beryllium is being made by electrolysis of a fused beryllium chloride-alkali chloride bath. The oxyfluoride process developed by Siemens and Halske in the 1920's has been abandoned because of the toxicity of the vapors given off.

Before World War II, the United States' supply of metallic calcium came from France, where it was made from the fused chloride by the "contact electrode" method (23). In 1939, the Union Carbide and Carbon Company started production by the same method at a plant at Sault Ste. Marie, Michigan (24), which is still in operation. The Pidgeon aluminothermic process is providing severe competition for the electrolytic method and would probably be favored if demand for this metal should increase.

Crude metallic cerium or "mischmetal" is being produced in the United States by electrolysis of fused alkali chloride-rare earth chloride mixtures (25) in plants at Niagara Falls, New York, and Edgewater, New Jersey. The improved high temperature properties of magnesium-rare earth metal alloys and other new applications may increase the demand for this metal in the near future.

Electrolytic indium (26) is probably produced by the Anaconda Copper Mining Company at its Montana zinc plants. Consolidated Mining and Smelting Company is using an electrolytic process at Trail, British Columbia.

There are plants for producing metallic lithium from the fused chloride at Maywood, New Jersey, and Minneapolis, Minnesota. The latter, constructed within the last five years, is a modern one and is now in process of expansion. A plant in Long Island City, New York, with four 8000–10,000 amp cells operated during World War II, but was shut down shortly thereafter. Lithium has interesting possibilities as an alloying metal. A 90 Mg-10 Li alloy has a body centered cubic structure and is more malleable, although not so strong as hexagonal magnesium alloys.

It is a well-known fact that the first large supply of uranium of sufficient purity to be used in nuclear reactors was made by a process developed by J. W. Marden and his associates at the Westinghouse Lamp Works, Bloomfield, New Jersey, namely the electrolysis of a solution of KUF_5 in a fused mixture of calcium and sodium chlorides, using a graphite anode and a molybdenum cathode (27).

Summing up, it is very evident that, even omitting aluminum and magnesium, the electrolytic metallurgical indust has enjoyed a very healthy growth in the last fifty years, h rosy prospects for expansion in the output of its presen products and the development of new ones, and can pri itself on producing quality products on a quantity basis. is a matter of special pride to the Society that many of th men who were responsible for this progress were membe of the Society and that some of them, Lawrence Addick Colin G. Fink, Anton Gronningsater, John W. Marden, an S. Skowronski, to name only a few, are still on its rolls.

REFERENCES

Unless otherwise noted, all references are to the TRANSACTIONS or the JOURNAL of The Electrochemical Society.

1. T. ULKE, **3**, 219 (1903).
2. S. HUGHES, *Eng. Mining J.*, **152**, No. 6, 72 (June, 1951).
3. M. F. HEBERLEIN, **77**, 119 (1940).
4. A. E. WHEELER AND H. Y. EAGLE, **74**, 375 (1938).
5. S. SKOWRONSKI, **51**, 139 (1927).
6. E. A. CAPPELEN SMITH, **25**, 193 (1914).
7. C. W. EICHRODT, **45**, 381 (1924).
8. H. Y. EAGLE, **45**, 365 (1924).
9. O. C. RALSTON, **51**, 129 (1927).
10. A. A. CENTER, *Trans. AIME*, **159**, 182 (1944).
11. G. H. CUNNINGHAM AND A. C. JEPHSON, *Trans. AIME*, **159**, 194 (1944).
12. U. C. TAINTON AND D. BOSQUI, **57**, 241 (1930).
13. J. J. FINGLAND, **57**, 177 (1930).
14. W. W. FOWLER, J. W. HANLEY, AND I. L. BARKER, *Mining and Met.*, **26**, 555 (1945).
15. R. PIONTELLI, **94**, 106, 377 (1946).
16. ANON, *J. Metals*, **4**, 589 (June, 1952).
17. C. L. MANTELL, **94**, 232 (1948).
18. E. B. SENGIER, *Eng. Mining J.*, **152**, 92 (Dec., 1951).
19. ANON., *J. Metals*, **191**, 17 (1951).
20. R. R. LLOYD, J. B. ROSENBAUM, V. E. HOMME, L. P. DAVIS, AND C. C. MERRILL, **97**, 227 (1950).
21. J. R. STACK, **45**, 441 (1924).
22. F. BENARD, *Trans. AIME*, **159**, 70 (1944).
23. P. H. BRACE, **37**, 465 (1920).
24. A. B. KINZEL, *Mining and Met.*, **22**, 488 (1941).
25. A. HIRSCH, **20**, 57 (1911).
26. L. R. WESTBROOK, **57**, 289 (1930).
27. J. W. MARDEN, **66**, 39 (1934).

A Half Century of Aluminum Developments

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The aluminum industry in America was founded upon the discoveries of Charles Martin Hall, namely, that substantial amounts of alumina could be dissolved in molten cryolite, and that the oxide of aluminum in this solution could be reduced electrolytically to metallic aluminum without decomposition of the molten cryolite. These discoveries, made in 1886, led to the formation of the Pittsburgh Reduction Company, and the first electrolytic production of aluminum started in Pittsburgh on Thanksgiving Day, 1888. The small company had made substantial progress and had reduction works at Niagara Falls, New York, and Shawinigan Falls, Quebec, when The American Electrochemical Society was founded in 1902. Charles Martin Hall was a charter member of this Society.

Just prior to Hall's invention, aluminum produced by chemical reduction of aluminum chloride with metallic sodium was selling for about $8 per lb. The Pittsburgh Reduction Company tried to sell its first electrolytically-reduced aluminum at $5 per lb but found few customers. Successive price reductions resulted in a widening of markets so that, by 1902, the annual production at the Niagara and Shawinigan Falls Works had increased to 7,478,000 lb. In 1902 the price of ingot aluminum, in 100-lb lots, was 35 cents per lb, and 33 cents in lots of 2000 lb or over. By this time it had become apparent that the future of the industry lay in securing more extensive markets. Many potential customers needed stronger alloys than those available and alloys with better

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resistance to corrosion. In 1907, the Pittsburgh Reduction Company had acquired a status which justified changing its name to Aluminum Company of America, a name now frequently shortened to Alcoa by press and public.

In the year 1915, the industry was trying to meet market demands with commercially pure aluminum and three or four wrought alloys and a similar number of casting alloys. However, in this decade there was developed in Germany an alloy called duralumin, which acquired greatly increased strength by a unique process of heat treatment. This alloy attracted the attention of the world by its performance in the airships of Count Zeppelin during World War I. Research was stimulated by this discovery and an investigation at the National Bureau of Standards resulted in a plausible explanation for the mechanism of heat treatment.

In the twenties, Alcoa's Aluminum Research Laboratories under the able direction of Francis C. Frary, Past President of The Electrochemical Society, originated a series of heat-treatable alloys with even wider application than duralumin. Another important development was the clad aluminum products in which the cladding electrolytically protected the core against corrosive attack. The first of these, developed by E. H. Dix, Jr., was known as Alclad and had a coating of pure aluminum and a core of heat-treatable aluminum-copper alloy. Another important development of Aluminum Research Laboratories was the production by William Hoopes and Francis C. Frary of aluminum of 99.99 per cent purity, by electrolytic refining. The Hoopes electrolytic cell employed a heavy aluminum-copper anode alloy on which was superimposed a lighter fluoride-base electrolyte with the pure aluminum floating on top and serving as cathode. Graphite electrodes served as cathode current leads.

Today, the industry employs some 25 wrought alloys in various forms such as plate, sheet, bar, extrusions, and forgings. A similar number of alloys find application in the production of castings. The strength of commercially available forms of aluminum has about tripled in fifty years.

In the year following the founding of The American Electrochemical Society, the Wright brothers flew a motor-driven, heavier-than-air plane for a distance of 852 ft. This plane's engine had a number of aluminum parts, but it was to be a long time before the airplane offered a substantial market for aluminum. The hope for such a market was encouraged by the performance of the Zeppelins, but it was not until the decade following World War I that the all-aluminum airplane became a commercial reality. The availability of strong aluminum alloys and investigations of structural design with aluminum have resulted in extensive application of this light metal not only in airplanes, trucks, automobiles, railroad trains, and ships, but also in bridges, plant equipment, and building construction.

American production was augmented by works erected at Massena, New York, Badin, North Carolina, and Alcoa, Tennessee. In 1926, a new Canadian works with a tremendous power reserve was started on the Saguenay River at a place called Arvida. In 1928, the aluminum works at Arvida and at Shawinigan Falls were transferred by Alcoa to a new and independent corporation named Aluminium Limited. By 1930, American production had nearly reached the 300 million-lb mark.

Hall's basic invention of electrolytically reducing alumina dissolved in molten cryolite has stood the test of fifty years' operation, and is still the process by which the world's supply of aluminum is produced. Obviously, however, there have been important developments in the equipment employed and in operational details. In Fig. 1 is shown an electrolytic cell of the type which was in use at Niagara Falls and Shawinigan Falls in that period. These were arranged in pot lines of about 100 cells carrying a current of about 12,000 amp. Today, pot lines are operating with currents of 50,000 to 60,000 amp, and the cells have increased correspondingly in size. A modern cell and a group of cells are illustrated in Fig. 2 and 3.

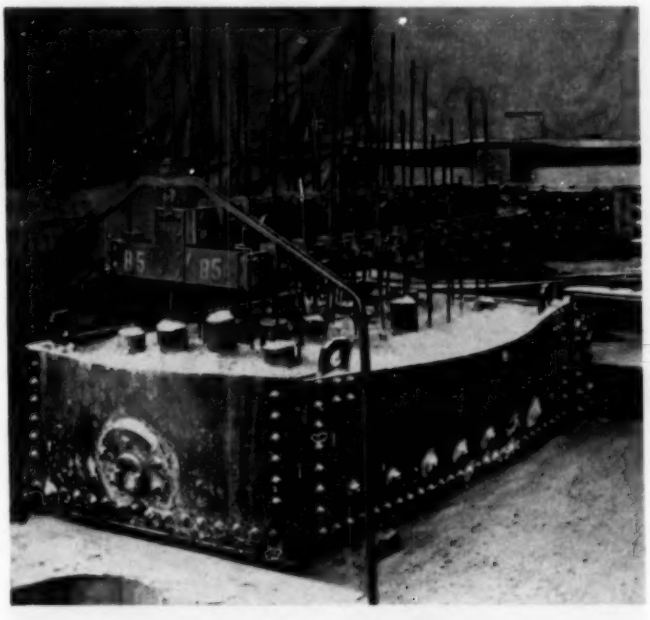

FIG. 1. Early type of Hall cell for the electrolytic reduction of alumina dissolved in fused cryolite bath.

FIG. 2. View of long line of modern type cells for electrolytic production of aluminum.

For many years, the aluminum was removed from the cell through a tap hole. A floor opening to hold the tapping crucible is shown in Fig. 1. Aluminum is removed from the modern cells by siphoning or pumping.

The passage of fifty years has marked interesting changes in the electric power supply for the production of aluminum. The first power contract at Niagara Falls, signed in 1893, was for mechanical power delivered by a rotating shaft, which operated a direct-current generator in the reduction works. As new hydroelectric installations began to supply power for aluminum, a-c power was delivered to rotary converters near the pot rooms. The mercury arc rectifier, when

a practical unit became available, was adopted generally by the aluminum industry. Today, about 1,750,000 kw of rectifiers are in operation in this service. The tremendous demand for aluminum, which developed during the World War II period, and the national power shortage, led Alcoa to initiate the use of natural gas engines for direct drive of d-c generators. The next step away from hydroelectric power is the building of a plant in Texas employing lignite as a fuel to make high-pressure steam to supply power for generating current for the reduction of aluminum. In 1951, approximately 4 per cent of the nation's electric power was consumed in the electrolytic production of aluminum.

FIG. 3. Top view of modern cell for electrolytic production of aluminum; rectangular baked carbon anodes and their supports are shown, together with bins from which alumina is fed to the bath.

The development of cells for the electrolytic reduction of aluminum can also be traced through the types of anode employed. Carbon anodes of high purity are required, because metallic impurities in the carbon are reduced and contaminate the aluminum. The conductivity, mechanical strength, resistance to oxidation, and other characteristics are impo tant in the efficient operation of the process, and have been given attention in developing satisfactory anodes. T cell shown in Fig. 1 employed prebaked cylindrical anod about 4 in. in diameter. With increase in cell capacity, t size of anode increased and the shape was eventually chang to anodes with square or rectangular cross section. The 19 anodes were supported by iron or copper rods either wedge or threaded in the upper end of the carbon anode. The lar modern rectangular anodes have a steel stub fastened in t head of the anode by cast iron; they are supported by a copp bar which is bolted to the stub and clamped to the anode bu Some 25 years ago, the Soderberg continuous, self-bakin anode was tried out by the aluminum industry and foun to have certain advantages. Through years of use the Sode berg anode has been improved, particularly with respect t the current leads and the method of support. At the prese time both prebaked and Soderberg anodes are used in pr ducing aluminum. Since approximately two-thirds of a poun of carbon is consumed per pound of aluminum produced, th electrode-carbon requirements of the industry are tre mendous.

In 1902, the production from a single cell was about 17 lb per day with a power consumption of over 12 d-c kwhr/l The modern units produce about 750 lb per day with a con sumption of about 8.5 d-c kwhr/lb. Of course, electric powe is required for other plant operations and values of 9 or 1 kwhr/lb are sometimes employed for calculating the over-a power requirements of the aluminum works.

In a little over fifty years, aluminum has risen in useful ness and volume to challenge for leadership among nonferrou metals. In the last eleven years two new concerns, the Rey nolds Metals Company and Kaiser Aluminum and Chemica Corporation, have become competitors of Alcoa as producer of aluminum in the United States. This is now the out standing electrochemical industry in point of power con sumption, and the United States and Canada are producing the major part of the world's aluminum requirements. The production in 1951 was approximately 1,283,000 *tons*, and by 1954 an annual production of over 2,000,000 tons is antici pated. The available reserves of ore give promise that alu minum can still look forward to a long period of growth.

Recent Developments in Alumina Electrolysis as Found in French and Italian Publications

F. V. Andreae[1]

During the years 1948–1950, under the chairmanship of Louis Ferrand, the third section of the Société française des Electriciens (electrochemistry, electrometallurgy, and electrothermics) devoted a number of meetings to the study of electrolytic solutions in molten cryolite in order to shed some light on the theoretical aspects of this electrolysis which is of such industrial importance. Appended to this summary is a list of the papers under consideration, (1–4), including the remarkable studies made by A. Vajna in the research laboratories of Mori during the last few years.

The following commentary deals particularly with the most recent articles which appeared in the January and February 1952 numbers of the *Bulletin* of the Société française des Electriciens.[2]

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Work of Dr. Darmois and Students

In works of varying importance E. Darmois of the Paris Faculty of Sciences, followed by some of his most recent students, Messrs. Doucet, Chalin, Rolin, Petit, Mergault, Zarzicki, and Miss Sutra has demonstrated the general applicability of Raoult's law, both to solutions of molten salts, at

[2] This publication is available through the Society, 14 Avenue Pierre-Larrousse, Malakoff, Seine, France. 400 French francs.

gh and low temperature, and to aqueous solutions (5) ovided that the saline medium possesses the fundamental operty of a pure solvent: that of melting at a constant mperature.

These experiments proved that Raoult's law is a limiting w which applies rigorously to the ideal solutions, which, in actice, are the very dilute solutions. This law is, therefore, ssible to direct observation only when the results of exrimentation are recorded with great exactness and absolute ecision, permitting accurate extrapolation.

Under these conditions (Raoult himself showed how to ply his formula) the molecular temperature drop for initely dilute solutions can be written $(\Delta t)/m = nK$; Δt repreents the measured drop in temperature in degree C of the elting point caused by the introduction of m moles of the lute in 1000 grams of solvent, K the cryoscopic constant, d n the number of dissociated ions.

This cryometric method is, therefore, simply a means of unting the dissociated ions and consequently of deterining the composition of complex ions which do not dissoate any further. The ions common to those of the solvent e the only ones that are not counted. This method is in mplete accord with recent conceptions, more particularly ith Debye's theory, in accordance with which the salt lutions must be considered as totally, or almost totally, nized.

One of Professor Darmois' students, Maurice Rolin (6–8), as very clearly developed the mechanism for the dissociation alumina dissolved in a bath of molten cryolite. The validity nd applicability of Rolin's observations were discussed at he December 21, 1950 meeting of the French Society of Electricians. There follows a summary of some of the perinent conclusions arrived at by Rolin.

The melting point of molten cryolite was found to be 006°C, or 1279°K. Since the molecular heat of fusions is 6.64 cal/g mole, Van't Hoff's formula permits the calculaion of its cryoscopic constant (40.8), which is verified by he cryoscopy of chlorides and fluorides.

The molecular state of molten cryolite is given by the quation:

$$AlF_6Na_3 \rightarrow AlF_3 + 3F^- + 3Na^+$$

nd that of dissolved alumina in the electrolytic baths by he two equations:

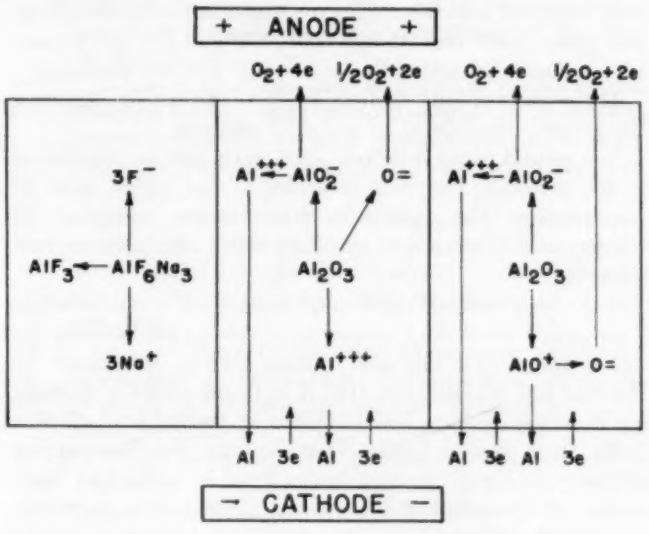
$$Al_2O_3 \rightarrow AlO_2^- + Al^{+++} + O^{--} \text{ (3 ions)} \qquad \text{(I)}$$

$$Al_2O_3 \rightarrow AlO_2^- + AlO^+ \text{ (2 ions)} \qquad \text{(II)}$$

he first equation applying to very dilute solutions (below 2%), the second to industrial concentrations.

Under normal operation, during electrolysis, only the alumina ions are discharged, while the cryolite, although ionized, does not participate in the electrolysis, and the appearance of Na^+-ions constitutes only a secondary and parasitic phenomenon.

The mechanism of electrolysis is illustrated in the diagram below, in which three compartments are shown. On the left is shown the ionization of nonelectrolyzed cryolite, in the center the discharge of the alumina ions at very low concentration, and at the right the dissociation of alumina at industrial concentration, by means of complex ions such as AlO_2^- at the anode and AlO^+ at the cathode.



In this last case one can assume that the electrolytic mechanism progresses as follows:

1. At the anode, an $O^=$ ion is discharged and the complex ion AlO_2^- is discharged to form O_2 and an Al^{+++} ion.

2. At the cathode, the AlO^+ ion forms Al^{+++} ion and $O^=$ ion, the former being discharged at the cathode while the latter must migrate to the anode.

Thus is explained the apparent anomaly of finding a cation Al^{+++} at the anode and O^{--} at the cathode and the complicated circuit which these ions have to travel to arrive at the end of the electrolytic process.

Actually there exists a general state of dissociation in accordance with the left and right thirds of the diagram (perhaps even with all three sections, at low concentrations), and it is simply the value of the applied potentials or the ionic concentration which determines which ions are discharged.

Contributions of A. Vajna

Special consideration must here be given to the work of A. Vajna (9–16), not only for the wealth and novelty of the physicochemical data presented to the electrochemists, but also for the originality of the experimental method employed, which included *direct observation* of the phenomenon under study. Special attention is called to the photographic reproductions made with the help of a microelectrolyzer (13, 15, 16).

Such a brief article must limit itself to a few remarks concerning two reports made by the author to the Société française des Electriciens, at its meetings of May 31 and June 4, 1951 (15, 16).

In the first paper the data on the critical current density confirm, with certain slight modifications, the results obtained by the Russian scientists Schiskin, Karpatchef, and Dolgof. The existence of this critical current density can be used to calculate directly the concentration of alumina dissolved in industrial baths. Mr. Ferrand has made an interesting application of this method in a new apparatus which predicts the anodic effect (17) and is especially useful with the continuous feeding of alumina which he proposes and of which more will be said below (18).

In his study of the capillary effects at the anode under normal and upset operation, Dr. Vajna concludes that the amorphous carbon is wetted in a molten cryolite bath of any composition only in the presence of oxygen. Since the wetting of the anodic surface is necessary to the passage of the cur-

rent, it follows that the oxygen must appear first at the anode, and that, under normal operation, CO and CO_2 are second ary products. Otherwise the bath would not wet the anode.

These observations confirm Rolin's conclusions regarding the *primary dissociation* of dissolved alumina.

The second paper does not reach such precise conclusions as the preceding one, and according to the author must be considered as the prelude to other studies regarding the kinetics of the secondary reactions which affect the current efficiency.

Some very unusual photographs taken on a microelectrolyzer clearly show the existence of a metallic fog between the two poles. Using the lead rinsing method suggested by Pearson and Waddington (19) it is found that the metallic fog is mostly sodium and is denser in neutral and alkaline baths than in acid baths. This explains why the current efficiency is higher in acid baths than in neutral or basic baths, other conditions being equal. This opinion regarding the nature of the metallic fog and the role it plays in the midst of the anodic gaseous phase is confirmed by Frejacques (4).

The second part of the paper is devoted to a tentative calculation of the diameter of the gas bubbles under the anode, under simplified assumptions. The author figures that the diameter is about 0.7 cm and is independent of the type of the bath and of the time of contact and the geometric shape of the anode.

Findings of L. Ferrand

Louis Ferrand, whose innovations in the field are widely recognized, spoke at the April 26, 1951 meeting of the Société française des Electriciens on the continuous dissolving of alumina (18), which in accordance with one of his patented processes (20) would practically eliminate the anode effect and replace manual or semimechanical methods of distributing alumina by entirely automatic methods.

At the June 19, 1952 meeting of the Société, Ferrand (21) presented his ideas regarding the properties of dilute electrolytes, with interesting remarks concerning the dissociation of alumina in baths of industrial concentrations, based on the latest publications (22).

All authors agree in recognizing the bad effects of the anode effect (23). To eliminate it completely, or at least to space it to the same rhythm as the tapping, would represent considerable progress and would result in a greater stability of operation, especially in the control of the temperature and a saving of the fluorine-bearing materials.

The discontinuous feeding of alumina makes use of the central free space in the case of prebaked electrodes (24), or of the peripheral space in the case of Soderberg self-baking electrodes.

The semicontinuous feeding, which is an alternative to the preceding method, does not require such large volumes of bath in order to get the same spacing of the successive anode effects, since it employs preventive feeding at regular intervals without waiting for the anode effect, and submits to the anode effects only at distant intervals. This method is in general use in the United States, Canada, and Russia.

At Kaiser's Tacoma Plant the cells are fed regularly every six hours. The anode effect is allowed to take place only when the cell becomes muddy. By this method an average of 0.6/0.7 disturbance per day is reached, or a disturbance every 36 hours. The same procedure is used at the Spokane plant where the disturbances are about 24 hours apart, considered too frequent. At the Reynolds Listerhill Plant the disturbances also occur about every 24 hours with feedings every six hours, one time on one side, the next on the other side.

Based on the conclusions reached by Dr. Vajna in studying the viscosity and conductivity of the bath (10, 11) Ferrand shows very clearly the disadvantage of this method of feeding, which is liable to result in alumina deposits on the conductive bottom when alumina is fed through the central opening. In any case this method results in a constantly changing alumina concentration which goes from a maximum of 7–8 per cent to a minimum of 1–2 per cent, passing suddenly from the minimum to the maximum at the time of feeding. This continuous variation of the concentration brings about a sudden drop in conductivity of the bath and of its temperature, followed by a slow rise in temperature and an increase in conductivity between two feedings, which naturally makes any control very difficult. It is to eliminate such disturbances and make automatic regulation of voltage and temperature easier that the author has developed the continuous oscillation of the anode, which permits a continuous feeding of the alumina. His work is based in part on the free fall speed of the alumina grains, as determined by Dr. Vajna (10). The linear motion of the anode at the surface of the bath is of the order of 3 mm/min (0.12 in./min) and the power to move the anodic equipment at this slow speed is about 1/2000 of the total power input; it is therefore negligible. On the other hand, manpower can be entirely eliminated if the alumina is fed by compressed air through a system of pipes which reach above the spaces between the anodes. During the test, the speed of the particles in the bath was about 0.11 gram/cm²/min, compared with 2.5–3 gram/cm²/min in the case of discontinuous feeding by means of a poker. The motion of the particles, therefore, is always much slower than the speed of free fall and there is no chance for the particles to reach the bottom before they are dissolved. Since the arrival of the alumina is also continuous, there are no dust losses.

Besides its important savings in manpower and energy, this method has the advantage of permitting, for a given interpolar distance, operation at a higher current density and, therefore, higher power input. This is because the control of the voltage at the terminal of the cell can be performed in a bath of low alumina content, constant temperature, and therefore of higher conductivity (about 12%).

With these baths approaching the conditions under which the anodic effect takes place, it is necessary to have a system which will predict the anodic effect. Such a system is described on page 100 of reference (18). This system permits the control of the speed or amplitude of the anodic oscillation, or both, so as to keep the alumina content constant. It is only necessary to adjust the current density in the pilot anode in such a manner that a signal be given when the alumina concentration has dropped, for example, to 0.2 per cent above the concentration at which the anodic effect will take place. The idea is to maintain at all times conditions of optimum operation which unfortunately are close to those at which the anodic effect takes place—a stop signal is therefore absolutely necessary.

Work of J. Bouchard

During the same April 26 meeting, J. Bouchard, after first presenting his personal views concerning the development of self-baking electrodes, discussed a few more special problems concerning the generation and evacuation of anodic gases (25).

Based on the studies of Dr. Vajna regarding the surface tension and the viscosity of the baths (9, 10), he tried to de-

termine the speed and the time of sojourn of the gases under the anode, and from there to suggest certain methods by which the path of the gases under the anode can be shortened, their evacuation facilitated, the time of contact lessened, and the current density increased.

Bouchard presents two possible solutions leading to improvements in the design of self-baking electrodes for high currents:

1. Cells with several anodes, which for 50,000 amperes would number four, each measuring 200 x 75 cm (80 in. x 30 in.) or a total of 60,000 cm² (9600 in.²). In such a design, the average path under the anode compared with one anode of 70,000 cm², which, moreover, cannot carry any larger current, is reduced from 37 to 16 cm. This design also permits the application of the Ferrand process of oscillating anodes and the use of continuous feeding of alumina, besides the automatic regulation with separate control of each anode. To apply this oscillating movement without too much power consumption would require passing the axis of oscillation through the center of gravity of the anode. This reduction of the anodic path, and the larger perimeter of the anodes should increase the liberation of the gases and increase the proportion of CO in the gases, retarding Boudouard's equilibrium and, therefore, reducing the carbon consumption. This is very important with self-baking electrodes, whose carbon baked at low temperature is more reactive, and has a tendency to increase the carbon consumption.

2. Cells with annular electrodes, as recently suggested by Ferrand, where several annular anodes (two or three), arranged concentrically around a central axis and individually controlled, permit both the increase of the interpolar distance from the periphery to the center, in the direction of gas liberation, and the control of the distribution of the total current among the various anodic rings. With such a design the Boudouard equilibrium is still more retarded than in the preceding case, not only because of the smaller mean path, compared to a round electrode of the same cross section, but mainly because of the higher speed at which the gases are liberated, and the shorter time of contact caused by the conical shape of the anodic surface and the forced withdrawal of the gases through the central chimney.

REFERENCES

All of the following articles except two are written and titled in French, but the titles have been translated for the convenience of the reader.

1. I. Cadariu, "Sur la tension électrolytique de décomposition de l'alumine." (The decomposition voltage of alumina). *Bull. soc. franç. Élec.*, 6th series, **74**, 531–539 (1947).
2. R. Gadeau, "Reflexions sur la théorie de l'électrolyse dans les cuves à aluminium." (Comments on the theory of electrolysis in aluminum cells). *Bull. soc. franç. Élec.*, 6th series, **74**, 540–544 (1947).
3. J. Bocquentin, "Contribution à la mesure de la tension d'électrolyse dans les cuves à aluminium." (A contribution to the measurement of the electrolytic potential in aluminum cells). *Bull. soc. franç. Élec.*, **99**, 677–683 (1949).
4. M. Frejacques, "Etat actuel des théories de l'électrolyse de l'aluminium." (Present status of the theories on the electrolysis of aluminum). *Bull. soc. franç. Élec.*, **99**, 684–692 (1949).
5. E. Darmois, "Les lois de Raoult et leur aspect moderne." (Raoult's laws and their modern applications). *Bull. Soc. chim. France*, 5th series, **17**, 1 (1950).
6. M. Rolin, "Cryoscopie dans la cryolithe fondue et l'ionisation de l'alumine et des oxydes dissous." (Cryoscopy in molten cryolite and the ionization of alumina and of dissolved oxides). Thesis. Paris. (1950).
7. M. Rolin, "Cryoscopie dans la cryolithe fondue et l'ionisation de l'alumine et des oxydes dissous." *Rev. mét.*, **48**, No. 3 (1951).
8. M. Rolin, "Cryoscopie dans la cryolithe fondue et constitution ionique de l'alumine dissoute." (Cryoscopy in molten cryolite and ionic composition of dissolved alumina). *Bull. soc. franç. Élec.*, 7th series, **13**, 35–46, D 47–55 (1952).
9. A. Vajna, "Tension de décomposition de l'alumine et mécanisme de l'électrolyse dans les fours industriels." (Potential of alumina decomposition and mechanism of electrolysis in industrial furnaces). *Alluminio*, **6**, 599–602 (1949).
10. A. Vajna, "Viscosité des bains d'électrolyse de l'aluminium à base de cryolithe à l'état de fusion." (Viscosity of electrolytic aluminum baths of molten cryolite). *Alluminio*, **2**, 135–145 (1950).
11. A. Vajna, "Sur la conductivité électrique des bains d'électrolyse de l'aluminium à base de cryolithe à l'état de fusion." (On the electric conductivity in electrolytic aluminum baths). *Alluminio*, **3**, 215–224 (1950).
12. A. Vajna, "Sur la densité des bains d'électrolyse de l'aluminium à base de cryolithe à l'état de fusion." (On the density of the electrolytic baths of aluminum dissolved in molten cryolite). *Alluminio*, **6**, 541–547 (1950).
13. A. Vajna, "Tensions superficielles des bains cryolithiques à l'état de fusion." (Surface potential of cryolite baths in the molten state). *Alluminio*, **1**, 29–38 (1951).
14. A. Vajna, "Mesures de la resistivité électrique des mélanges alumine-cryolithe à l'état solide." (Measurements of the electrical resistivity of mixtures of alumina-cryolite in solid state). *Alluminio*, **2**, 147–149 (1951).
15. A. Vajna, "Tension d'électrolyse de l'alumine en régime normal et en régime trouble dans les bains d'électrolyse à base de cryolithe à l'état fondu." (Voltage for the electrolysis of alumina in normal and disturbed states in electrolytic baths of molten cryolite). *Bull. soc. franç. élec.*, 7th series, **14**, 85–91 (1952).
16. A. Vajna, "Facteurs physiques de rendement de courant dans les bains d'électrolyse à base de cryolithe à l'état fondu." (Physical factors in the current efficiency in electrolytic baths of molten cryolite). *Bull. soc. franç. élec.*, 7th series, **14**, 92–96, (1952).
17. L. Ferrand, "Note sur un nouveau dispositif de signalisation d'effect d'anode." (Note on a new apparatus for signaling the anodic effect). *Bull. soc. franç. élec.*, **14**, 100, (1952).
18. L. Ferrand, "La mise en solution continue de l'alumine dans la fabrication de l'aluminium." (Continuous dissolving of alumina in the manufacture of aluminum). *Bull. soc. franç. élec.*, 7th series, **14**, 97–100 (1952).
19. T. G. Pearson and J. Waddington. Electrode Reactions in the Aluminous Reduction Cell. *Trans. Faraday Soc.*, **1**, 307–320 (1947).
20. L. Ferrand, U. S. Pat. 2,061,146, Dec. 3, 1934 and 2,560,854, July 17, 1951.
21. L. Ferrand, "Caractéristiques des électrolytes à faible teneur en alumine." (Properties of electrolytes with low alumina concentration). *Bull. soc. franç. élec.*, 7th series, **20**, pp. 477–480, Aug. 1952.
22. Melle G. Sutra and E. Darmois, "Nature de la dissociation de l'alumine dissoute dans la cryolithe fondue." (On the nature of the dissociation of alumina in molten cryolite). *J. Phys. Radium*, 97–98 (1951).
23. Francis C. Frary, "Electrolytic production of aluminum," *J. (and Trans.) Electrochem. Soc.*, **94**, 33 (1948).
24. F. C. Frary, op. cit., Fig. 2, p. 35.
25. J. Bouchard, "Perspectives nouvelles pour le developpement des anodes Soderberg dans la fabrication de l'aluminium." (New perspectives in the development of Soderberg anodes in the manufacture of aluminum). *Bull. soc. franç. élec.*, 7th series, **14**, 101–111 (1952).

A Review of Magnesium Production and Uses

W. S. Loose[1]

The magnesium industry in the United States had its beginning only 36 years ago. Many persons, members of The Electrochemical Society, still active in the industry today, were present when the U. S. magnesium industry was born.

Stimulated by the demand for the metal during World War I, five companies were engaged in magnesium production in 1915. After the armistice, the struggle for survival of the industry began and, in 1920, only two producers were left. In 1927 one of these companies ceased operations and The Dow Chemical Company has remained the sole producer, except for the period between 1942 and 1945 and the present Korean crisis.

While present interest in magnesium is largely concerned with national defense, a wide number of commercial applications have been developed. Many of the present military applications have counterparts in commercial fields, and experience and knowledge gained from these military applications can readily be applied to civilian use.

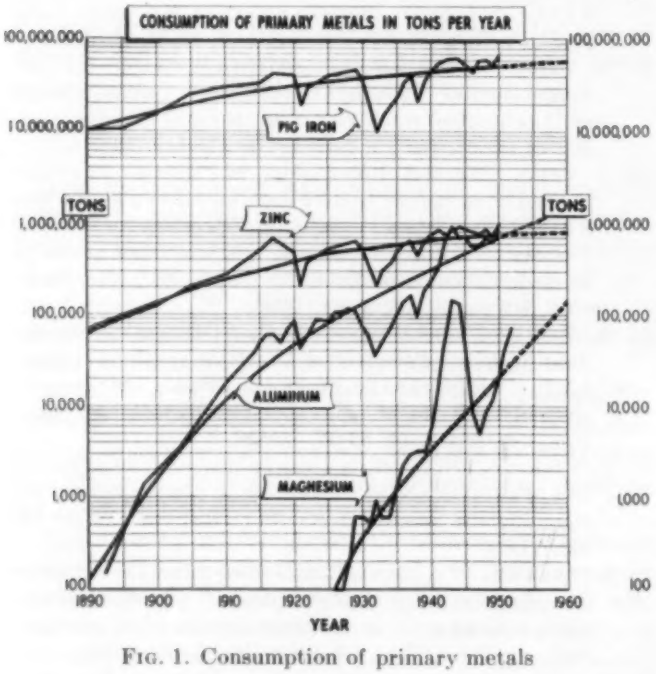


FIG. 1. Consumption of primary metals

Consumption of the metal in the past year reached a total of about 100 million lb, and, projected on an average growth rate curve, it is possible that 300 million lb will be consumed in 1960.

In 1940, all domestic production was from the electrolysis of magnesium chloride extracted from subterranean brines at Midland, Michigan. In early 1941, The Dow Chemical Company started operations at Freeport, Texas, converting sea water to magnesium. In essence, the sea water is limed to precipitate magnesium hydroxide which is converted to magnesium chloride and then electrolyzed to produce molten magnesium.

Magnesium exists in practically infinite amounts in the oceans of the world, providing a virtually unlimited source of supply. It has been estimated that if magnesium were taken from the seas at the rate of 100 million tons per year for one million years, the magnesium content would be reduced from 0.13 to 0.12 per cent—if no more had washed into the sea in the meantime.

Continuous research and development have led to new and improved processes, designs, and alloys.

Fig. 2. Close-up of the electrolytic cell for the production of magnesium.

FIG. 3. B-36 Consolidated Vultee's giant bomber represents the largest single use of magnesium. Crosshatched portion shows the external use of magnesium on the aircraft.

In the field of alloys, probably the most significant developments have taken place in the use of rare earth elements to provide magnesium alloys with improved properties at elevated temperatures. These alloys are commercially available and are finding wide application in jet engines for newer aircraft.

An extrusion alloy of magnesium containing zirconium was used in special aircraft extrusions during World War II

[1] Magnesium Department, The Dow Chemical Company, Midland, Michigan.

and has since become a commerical extrusion alloy. This alloy provides a combination of the highest yield strength and toughness.

Magnesium can be given a variety of decorative and protective finishes by such common methods as chemical treatments, anodizing, painting, and electroplating. The development of such finishing schedules has greatly accelerated the use of magnesium parts in many applications.

The electroplating process for magnesium, perfected in the last few years, is perhaps the most significant finishing development. The process consists of the deposition of an initial zinc coating by immersion, followed by a copper flash, and electroplating in the standard plating baths.

Anodic treatments for magnesium provide hardness and abrasion resistance. They can be painted and some of the treatments can be dyed.

Chemical treatments are applied to magnesium for protective or decorative purposes. Basically, all chemical treatments provide some protection against corrosion during shipment, storage, and use.

At the present time, major applications of magnesium lie in the military field.

The largest single field of application for magnesium today is in aircraft. Consolidated Vultee's giant B-36 bomber uses some 9000 lb of the metal in the airframe alone, and an additional 6670 lb in engines, wheels, gun turrets, and miscellaneous parts.

Another large aircraft application is the Sikorsky S-55 helicopter. With the exception of a few small areas, the entire fuselage of this 10–12 passenger aircraft is magnesium sheet. In addition, 90 castings of magnesium are used on the aircraft.

Perhaps the newest field of large application of magnesium is automotive. The automotive industry, using quantities of magnesium die castings, represents a large present market and one with tremendous potential.

A huge field is being developed in the cathodic protection of pipelines, water heaters, boiler type equipment, and ships. This field, depending on the high solution potential of magnesium, is just beginning to be explored. A related use of magnesium is as the anode in dry cell batteries. It shows an increased capacity over conventionally used materials.

The unique combination of strength, lightness, and stability has made magnesium one of the common structural metals. The chemical and metallurgical uses provide other fields of application. The virtually unlimited source of supply proves a more significant factor as reserves of easily available and reducible ores of other metals are depleted.

Production of Metallic Sodium

Harvey N. Gilbert[1]

Sodium was produced in small amounts by thermal methods from the time of Deville about 1860. A new process was developed by Hamilton Y. Castner and a plant built in Oldbury, England, just prior to the discovery of the electrolytic process for the production of aluminum by Hall.

Since the sodium was to have been used for the production of aluminum by reduction of aluminum chloride, this process could not compete with the electrolytic aluminum process, and Castner was forced to develop other uses for his sodium. He quickly worked out a process for converting sodium into sodium peroxide and, encouraged by the success of the electrolytic aluminum process, began experimenting with an electrolytic sodium process. The Castner electrolytic process, patented about 1890, marked the birth of the electrolytic sodium industry and the next 50 years represent its growth and development both as to processes and uses for sodium.

The Castner Process

In this process, sodium was produced by the electrolysis of fused caustic soda. The cell consisted of an iron vessel mounted in a brick-work furnace so that it could be externally heated. The cathode was located in the center and was surrounded by a nickel anode which was suspended from above. The early cells operated on 1200 amperes at 5 volts. Later developments carried on by the Niagara Electrochemical Company at Niagara Falls, New York, resulted in a 7000-ampere cell operating at about 4.3 volts. This larger cell did not require external heating. The anode was an iron ring cast integrally with the concentric iron shell of the pot. The cathode was an iron cylinder located within the anode, and was mounted vertically on a heavy copper pole which entered the cell from below through a neck in the cell bottom. It was insulated from the cell body by a layer of frozen bath. The anode connection was made with the shell, and both anode and cathode connections were made in a pit beneath the working level of the cell.

An iron gauze diaphragm was suspended from a casting which rested on the top of the cell and was insulated from the shell. This casting contained a cylindrical pot just above the diaphragm, which served as a collecting reservoir for the sodium. The collecting pot was covered by an iron cover which could be removed to bail out the sodium. The cover contained a small hole through which hydrogen escaped and burned. In the latest form of the cell, a solid cover was used and hydrogen was collected and removed through a pipe entering the chamber beneath the cover.

The success of the larger cell was dependent on the use of heavy nickel plating which was applied to the surfaces of the anode and cathode, and collector parts. The deposition of thick layers of nickel which would stand such severe conditions was itself an achievement in those days.

The initial electrolyte consisted of a mixture of caustic soda and sodium chloride, the salt being added to improve the conductivity. As the cell aged, the NaCl and Na_2CO_3 content of the bath increased until it was necessary to shut down the cell and start with fresh bath. Caustic soda from the Castner mercury cells was used for feed. Such caustic was low in NaCl. The discarded bath was dissolved in water and the caustic values recovered and sold. This procedure prevented the buildup of metallic impurities in the bath.

The operating temperature was held at slightly above the melting point of the bath, about 310°–320°C. The reactions of the cell may be given as:

$$4\ NaOH \longrightarrow 4\ Na^+ + 4\ OH^-$$

$$4\ OH^- \longrightarrow 2\ H_2O + O_2$$

$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2.$$

[1] Cayuga Drive, Niagara Falls, New York.

From this it is seen that half the sodium which is initially produced is lost by reaction with the water formed at the anode.

Hydrogen and sodium are produced at the cathode and oxygen at the anode.

Various attempts were made to increase the yield by diverting the water to other compartments before it could react with the sodium and also by variations of the cell bath, but no commercial cell employed these modifications. In practice, therefore, the Castner cell had a current efficiency of 40 to 50 per cent in sodium production, and this low efficiency, in addition to the higher cost of the raw material NaOH as compared with NaCl, caused workers to search for a process which would electrolyze NaCl directly. Such a process would produce chlorine as a by-product.

The Castner process has not been used in this country since 1925, but is still used abroad.

Operating Difficulties

The problem of the electrolysis of NaCl was studied as early as 1890. The difficulties in operating such a bath were tremendous. The melting point of salt is about 805°C, at which temperature the vapor pressure of sodium is nearly half an atmosphere, the solubility of sodium in the bath becomes appreciable and there is a tendency to form metal fog. All these factors, together with the excessive corrosion at higher temperatures, made the task a formidable one.

The problem is further evidenced by the issuance of nearly 100 patents in this country and the commercial success of but one of these. The Acker process used a bath of fused NaCl with a molten lead cathode to produce chlorine and a sodium-lead alloy. The alloy was subsequently hydrolyzed by steam in a separate compartment to form fused anhydrous caustic. The process was operated at Niagara Falls from about 1900 until 1907 when the plant burned down and it was discontinued.

While considerable work was done by others to remove sodium from sodium-lead alloy, no commercial process resulted and attention was directed toward the use of baths consisting of NaCl and other salts which would lower the melting point.

Seward and Von Kugelgen worked with a mixed bath in a cell at the Virginia Electrolytic Company from 1904 to 1914 when work was discontinued.

It is interesting to note that two of the men associated with the Acker process went on to develop the fused salt process. R. J. McNitt developed a cell which was operated for a short time during the first world war by the Roessler & Hasslacher Chemical Company at St. Albans, West Virginia. It was discontinued because of a number of operating difficulties. The problem was ultimately solved by another former Acker process man, J. C. Downs who, with his associates at the Roessler & Hasslacher Chemical Company at Niagara Falls, developed the present cell. The Downs cell is now used, with various modifications, by three companies in the United States and in several European countries.

This cell represents engineering of a high order and, with modern materials of construction, has produced a commercial process for the production of sodium and pure dry chlorine from salt.

The Downs cell consists of a cylindrical iron shell with a firebrick lining. A graphite anode enters through the center of the cell bottom. The cathode is a cast steel ring which surrounds the anode and is supported by two lugs which emerge through the iron shell, 180° apart.

Insulation of the anode and cathode from the shell is accomplished by a layer of frozen bath. A metal conical dome is suspended above the anode and the bottom edge of the dome supports an iron gauze diaphragm which is spaced equally between the anode and cathode and extends to the lower level of the cathode. The interior of the dome above the bath level is lined with a firebrick composition.

The casting which forms the dome is extended beyond the diaphragm support to form an annular inverted trough which inclines toward a vertical riser pipe at the high point of the trough. In operation, chlorine is formed at the anode and rises between the anode and the diaphragm to the central dome from which it passes to the mains. Sodium is formed at the cathode, rises to the collecting trough which is located directly above it, and passes out into a collecting vessel where it cools, is removed at intervals, and taken to a separate location for purification.

The purified sodium is then cast into bricks or run directly to processes for conversion into sodium peroxide and sodium cyanide. The liquid sodium is also run into special sodium tank cars (over 80,000 lb capacity) where it is solidified by cooling and shipped to consumers.

Salt which has been treated to remove impurities, such as sulfur and oxygen-containing salts, is fed to the cells. The cell bath contains calcium chloride which lowers the melting point. The chlorine is dry and can be maintained at high purity because of the relatively compact and closed central collecting system.

The raw sodium contains some calcium metal, most of which is removed by the purification system which produces a product containing less than 0.04 per cent calcium metal as the principal impurity.

From time to time the diaphragms become worn or corroded and are replaced by lifting out the dome casting. The cell life is well over a year before wear of the anode increases the spacing between it and the cathode, and consequently increases operating voltage. When this occurs, the cell is shut down and rebuilt.

Operating data on similar cells in Germany are given by W. C. Gardiner in Technical Industrial Intelligence Branch, U.S. Department of Commerce, FIAT Final Report 820 (P.B. 44671) June 20, 1946. This mentions cells of 24,000- to 32,000-ampere capacity which use as electrolyte a mixture of 58–59 per cent $CaCl_2$ and 41–42 per cent NaCl. The operating temperature is stated to be 590°–595°C.

Uses of Sodium

Historically, the first commercial use of sodium was for the manufacture of sodium peroxide; this process has been improved and still represents an important outlet for sodium. Other uses: sodium cyanide was developed from sodium in the early 1890's; sodium is used for the manufacture of indigo and as a reducing agent in organic preparations; large amounts of sodium are used in the preparation of tetraethyl lead and for the reduction of fatty esters; sodium is reacted with hydrogen in a fused caustic bath to form sodium hydride which is used to descale stainless steel and other alloys.

Further uses will be developed as the specific properties of sodium are appreciated. Much progress has been made in its safe handling. Molten sodium can be handled as any other liquid if kept out of contact with air. It can be pumped and filtered. While most of its applications have been as a chemical reagent, under proper conditions its ability to conduct heat and electricity are beginning to be utilized. Truly, sodium has become a mature individual in the past 50 years.

The Chlor-Alkali Industry, 1902-52

Deane O. Hubbard[1]

When The Electrochemical Society was founded in 1902, the electrolytic chlor-alkali industry in this country was but a small youngster, ten years of age. That year there was in operation a total of five chlor-alkali plants, with a combined output of less than forty tons of chlorine per day. In 1952, these five plants, or their direct successors, are still producing chlorine and caustic. One of them, the Dow Chemical Company of Midland, Michigan, is now the largest producer of chlorine in the United States. Another, the Brown Chemical Company of Berlin, New Hampshire, is the successor of the original installation in this country.

The original plant of bell jar cells was installed in 1892 at the Electro Chemical Company in Rumford Falls, Maine. These first cells were soon replaced with a horizontal diaphragm cell developed by Ernest LeSueur and Charles N. Waite. In 1898 this chlorine plant was moved to what is now the Brown Company plant in Berlin, New Hampshire, where enlarged and improved LeSueur cells are still in operation, although some of them have been replaced with and the plant further expanded with the Hooker type S cell.

In 1895, another of that original group, the Mathieson Chemical Corporation installed the first Castner cells at Saltville, Virginia. In 1897, this installation was moved to Niagara Falls, New York, where the company still operates a modified and improved version of the original cell which was a rocking-type mercury cell. Recent installations by Mathieson at their Saltville, Virginia, and their McIntosh, Alabama, plants use a horizontal mercury cell of their own development.

The other two of that original five still in operation after more than fifty years are the S. D. Warren Company at Cumberland Falls, Maine, and the Niagara Alkali Company, which started as the Roberts Chemical Company in Niagara Falls, New York.

During this fifty-year period the chlor-alkali industry has expanded from these original five to 63 plants, operated by 38 companies. Fifty years ago the daily production was less than 40 tons per day; today the output is over 6000 tons per day, with new plants in the process of construction and further expansions scheduled.

The producing unit of the chlor-alkali plant is, of course, the electrolytic cell in which sodium chloride is electrolytically decomposed to produce chlorine, sodium hydroxide, and hydrogen. It is essential that the chlorine and sodium hydroxide are kept separated after they have been produced. This has been accomplished by two basic methods. One is by means of a diaphragm, placed between the anode and cathode, through which the brine flows carrying the sodium ions from the anode compartment where the chlorine is produced, into the cathode compartment where hydrogen is released, leaving sodium hydroxide in solution. The mixed sodium hydroxide-brine solution flows from the cathode compartment. Subsequent evaporation concentrates the sodium hydroxide and separates the salt.

The second method of keeping the chlorine and the sodium hydroxide separated is by the use of mercury. In the mercury cell the chlorine is released at the graphite anode. Sodium is plated in the mercury cell to form an amalgam. By mechanical means the amalgam is passed into a decomposer where it is contacted with water in the presence of short-circuited graphite electrodes in the two liquid phases. Thus the sodium reacts with water, producing sodium hydroxide and releasing hydrogen. Sodium hydroxide up to 73 per cent concentration can be produced in suitable decomposers.

Diaphragm cells have had a variety of shapes, sizes, and materials of construction, but the diaphragms have always been based on asbestos fiber used as paper, cloth, or fiber. The first diaphragm cell used in this country, known as the LeSueur cell, used a horizontal paper diaphragm over the horizontal cathode screen. The cell is a square or rectangular box with the cathode laid out in a very shallow V in the bottom. Glass rods placed on the diaphragm serve to support the anode graphite blades and maintain the proper spacing as the graphite wears away. The top of the box is closed with slabs of concrete or other suitable materials. Where intermediate supports are required bricks are stacked on the diaphragm.

Another early diaphragm cell which was used with success in its original and subsequent forms was proposed by C. P. Townsend. With the assistance of Elmer A. Sperry, Townsend's ideas were successfully developed to the point of trying a plant scale cell. In 1905, with financing by the Elon H. Hooker's Development and Funding Company, later the Hooker Electrochemical Company, Townsend's laboratory cell was developed for commercial use.

The cell was of the vertical type with a long, high central row of graphite anodes. Opposing the anodes on either side of the cell was a paper diaphragm backed up with a wire screen cathode. The cell was operated with the compartment behind the screen flooded with kerosene to regulate the brine flow through the diaphragm and to separate the caustic liquor from the cathode, preventing back migration. The flooded cathode compartment is still used in the Hooker cells, although the use of kerosene was discontinued even before the Townsend cells became obsolete.

The original paper diaphragm of Townsend's was soon replaced with an impregnanted asbestos cloth diaphragm developed by Leo Baekeland. The impregnant consisted of a mixture of iron oxide, asbestos fiber, and colloidal iron oxide. When the flow through the diaphragms became too low they were scrubbed clean and reimpregnated. In 1925 Kenneth E. Stuart began work on the development of an asbestos-fiber diaphragm deposited directly on the cathode screen by vacuum. Subsequent success permitted cathode shapes that were not readily adaptable for paper or cloth-covered diaphragms.

To use the deposited diaphragm Stuart designed a cathode consisting of a series of vertical envelopes, called fingers, made of a heavy wire close mesh screen. The fingers were equally spaced along a base plate and perpendicular to it. Assembled in the cell the fingers are in vertical parallel planes. At the root of the fingers is a collector space to accumulate and remove the caustic cell liquor and hydrogen from the fingers and their cathodic surface. This cathode was initially used in a modified Townsend cell known as the Marsh or type E cell. It was long and narrow with the root of the fingers and backing plate forming the side of the cell. The bottom of the cell was arranged to hold a series of graphite plates placed vertically to mesh between the cathode fingers. Thus, instead of two relatively large plane surfaces opposing each

[1] Hooker Electrochemical Company, Niagara Falls, New York.

other as the cell electrodes, the cell was in effect a number of separate units operating in parallel within a single container.

Having produced a deposited diaphragm and modified a cell to utilize it where it was commercially proven, Stuart proceeded to design a cell around the diaphragm. To conserve heat, the cathode fingers were designed to extend perpendicular from two sides of an approximately square channel frame. The graphite blades are set in molten lead to form 15 vertical rows of blades down each side of the cell. That assembly, set into a shallow pan-shaped concrete casting, served as the anode assembly and cell bottom. Contact is made through a copper bar, set in the lead and extending through one side of the concrete bottom. The top is a hollow concrete casting in the shape of a truncated pyramid.

The type S cell originally designed for 6000 amp was first installed for commercial use at Hooker's Niagara plant about 1935. It soon proved itself to be better than expected and was used for plant expansions by Hooker and licensed for use at competitors' plants. During World War II, it was accepted extensively by the federal government agencies for the Arsenal chlorine plants and a number of Defense Plant Corporation plants. The cell is now being operated at 10,000 to 12,000 amp in several plants.

In response to the need for larger cells, the writer, using type S cell data and experimental data from two modified type S cells, designed the type S-3 cell for operation at about 20,000 amp. The type S-3 cell has twice the active anode and cathode area of the type S cell and used the same design principle. In June of 1948 the first circuit of type S-3 cells went into operation. In 1951 a modification of the type S-3 cell, known as the type S-3A cell was placed in commercial operation. Externally it has been designed for current carrying up to 30,000 amp. Several circuits of type S-3 and type S-3A cells are in commercial operation.

Some of the other well-known diaphragm cells are the Hargraves-Bird, Nelson, and Allen-Moore. These are all vertical diaphragm cells with graphite rows down the center of the cell, similar to the Townsend cell. The Nelson cell was fairly shallow while the others were high like the Townsend cell. In contrast to the Townsend cell, however, they all used empty or drained cathode compartments. In the Hargraves-Bird cell, carbon dioxide was added to the cathode compartment to produce sodium carbonate.

Another group of cells, associated with the names of Vorce, Wheeler, and Tucker-Windecker, are vertical cylindrical cells. In these the graphite blades are long and narrow, being suspended from the top. Around the ring of graphites is a perforated steel cathode plate faced with an asbestos-paper diaphragm.

At the Dow Chemical Company, cell development work has centered around a bipolar cell. The original bipolar cells consisted of graphite plates mounted in a frame. In the same frame, backed up to the graphite anodes was a cathode faced with an asbestos-paper diaphragm. Racked up in proper order like a filter press, the compartments operated in series as a bipolar cell.

In Dow's latest cell, the cathode is constructed as a series of vertical envelopes or fingers, similar to the Hooker cells. From the opposing anode frame the anode graphite blades are perpendicular to the base plate and placed so that they will mesh with the cathode fingers. The anode of the second section is backed up to the cathode of the first section. With successive sections fitted together in series, a high capacity bipolar cell results.

The mercury cells for the production of caustic and chlorine release chlorine in the cell, plating sodium into mercury to form an amalgam. The amalgam is moved from the electrolytic section of the cell into another compartment for decomposition. There the amalgam is contacted with water in the presence of graphite electrodes contacting both liquids. With the major portion of the sodium stripped from it, the amalgam is returned to the electrolytic cell.

The Castner, or rocking cell, which was the basis of the Mathieson chlorine plant, is a three-compartment cell. The central compartment is the electrolytic section; sodium is recovered in the two end compartments. When the cell, which is balanced in the center, is rocked, the amalgam flows back and forth between compartments. Thus, the amalgam is alternately strengthened with and stripped of sodium. This original design has through the years been improved and modified at the Mathieson Niagara Falls plant, to meet modern competition.

As evidenced by their more recent installations at Saltville and at the new plant in Alabama, Mathieson's cell development work has deserted the rocking cell in favor of the horizontal cell which flows the mercury over a wide, slightly inclined plane surface under the anode plates. At the end of the cell, the amalgam formed flows into a decomposer of which the most popular form today is a vertical tank filled with graphite.

In the early days, cell development followed the familiar pattern of developing an idea from extremely limited knowledge and then proceeding to experiment until a successful cell resulted. The method was surely more art than science. During the past fifty years, the theories of electrochemistry, ion movements, and other basic tools of the industry have been vastly expanded. Nevertheless, even though cells can be designed from theoretical calculations, an extensive personal knowledge is required and radical departure from pioneer basic styles requires extensive laboratory and plant scale testing.

During the fifty years that The Electrochemical Society has been in existence, not only chlorine cells, but methods of handling chlorine have undergone extensive changes. In the early days of the industry, chlorine was converted into chlorine water and sodium hypochlorite for bleaching uses. Later, chlorine was dried with sulfuric acid and converted to bleaching powder. As the years passed, means of compressing chlorine were sought. One early attempt at the solution of this problem was a type of hydraulic ram which had some success.

The development of the Nash turbine using sulfuric acid as the sealing liquid was a major contribution, making pressures sufficiently high for liquefaction possible. By this means the shipment of chlorine was greatly facilitated, thus opening up more potential uses for chlorine and strengthening a weak market. About 1937 reciprocating compressors with carbon rings were tried successfully in commercial use. They opened the way to higher pressure compression.

In the early days of chlorine-caustic production, the demand was for caustic. However, electrolytic-cell production has no regard for market requirements. It makes chlorine and caustic in an unfailingly constant ratio. In general, during the fifty-year period, uses for chlorine and caustic have balanced out remarkably well, but there have been times frequently throughout the years when the uses, like the swing of the pendulum, have been out of balance on one side or the other.

While caustic soda can be fused and stored in light steel drums, chlorine requires high-pressure storage tanks which are expensive. Therefore, since chlorine use or sales usually control the plant operating rate, most of the research has been to find further uses for it. The research chemists and engineers have been so successful in that line with their insecticides,

lubricant additives, fire-resistant and noncombustible solvents, and plastics that the present sales trend is for more chlorine.

Having developed a short review of the past fifty years in the chlor-alkali industry, one cannot help but wonder what changes may come in the next fifty years. A glance at the trends in plastic materials may be a key. Certainly they will have noticeable effect on cell design in the near future, and probably a radical effect as the fifty-year period advances. The present trend is in the direction of larger capacity cells. That will certainly continue in the future. Fifty years ago one had a vague and probably unscientific idea and proceeded to develop it, successfully or otherwise. Today, one has scientific data to aid in cell and equipment design. With scientific knowledge developing at an accelerated rate and technical societies continuing to assist in the distribution of that knowledge, just as The Electrochemical Society has been doing for the past fifty years, one can venture to predict that the technical aspect of the chlori-alkali industry will continue in its rapid advancement.

Progress in the Electrolytic Manufacture of Chlorates and Perchlorates in the United States and Canada Since 1902

Walter Wallace[1]

The electrolytic manufacture of chlorates began in the United States at the close of the last century following the protective tariffs of 1894 to 1897.

In 1897, the National Electrolytic Company of Niagara Falls, New York, operating under the United States patents of W. T. Gibbs, commenced the manufacture of potassium chlorate, and about the same time the North American Chemical Company, of Bay City, Michigan, began the manufacture of potassium and/or sodium chlorate by a process similar to that used by their parent company, The United Alkali Company, in England. In 1899, Oldbury Electro-Chemical Company, of Niagara Falls, started manufacture of potassium chlorate with a process similar to that of their parent company, Albright & Wilson Limited, of Oldbury, England

While the cells used in these processes were mechanically different, the electrochemical efficiencies were approximately the same, and all of them used platinum anodes and copper cathodes.

The total production in the United States at that time was approximately 750 tons of sodium chlorate and 5000 tons of potassium chlorate per annum.

By the summer of 1903, Oldbury Electro-Chemical Company was manufacturing only sodium chlorate, while North American Chemical Company manufactured both.

The principal use of potassium chlorate was in matches, but it was also used in pharmaceuticals to a small extent, in the manufacture of certain explosives, and in the generation of oxygen. Sodium chlorate was used principally in the textile industry and in color manufacture, mild farm explosives, and also to a small extent in the generation of oxygen.

Oldbury Electro-Chemical Company commenced the manufacture of potassium perchlorate in 1910, with the yearly production of 150 tons used in railway signal fusees and pyrotechnics. Until this time the potassium perchlorate had all been imported.

The situation regarding chlorates continued with a slow increase in production and consumption under the continued protection of the Payne-Aldrich Tariff, and substantially all chlorates and perchlorates used in the United States for some years prior to World War I were of domestic manufacture. During the first decade of the century there were improvements in cell efficiency with lower power consumption which were common in the industry.

[1] Oldbury Electro-Chemical Company Niagara Falls, New York.

The Payne-Aldrich Tariff was 2 cents a pound on potassium chlorate, 1½ cents a pound on sodium chlorate, and 25 per cent ad valorem on potassium perchlorate. The Underwood Tariff of 1913 reduced these rates to ½ cent a pound on each of the chlorates and to 15 per cent on perchlorate, and strong foreign competition was beginning to be felt when World War I started.

Although there were demands on the United States during the war for additional production for export to replace supplies in other countries formerly obtained from Europe, the production of potassium chlorate was limited by the scarcity of muriate of potash also supplied from Europe, and this condition continued throughout the war. On the other hand, there was increased production of sodium chlorate, it being used in some instances as a substitute for the potash salt and, also, considerable quantities were exported.

Oldbury Electro-Chemical Company had eliminated platinum as electrode material for chlorate sometime before the war started which made rapid expansion of its sodium chlorate plant quite economical.

With the end of the war, the inadequate duty of ½ cent a pound imposed by the Underwood Tariff on chlorates began to be felt in the United States, and chlorates were imported in large quantities. Quoting Williams Haynes (1), "During the 20's sodium and potassium chlorates had a turbulent career, ending in a humiliating climax. When the demand shrank to present time uses, chiefly in match heads and pyrotechnics for potassium chlorate and textiles for sodium chlorate, Europeans made determined efforts to recapture the American market. Although the tariff commission ordered investigation of comparative costs and the tariff was advanced, it was too late or inadequate."

Prior to the war, imports of potassium chlorate and potassium perchlorate together (no separate figures were kept until 1926) were of minor importance, and even in 1913 there were only about 600 tons imported, with consumption of about 6000 tons of potassium chlorate and 150 tons of potassium perchlorate. With the end of the war and the resumption of shipping, the imports from Europe of potassium chlorate into the United States jumped to 1000 tons in 1921, 4400 tons in 1922, and 4500 tons in 1923, despite the increase in duty under the Fordney-McCumber Tariff of 1922, which increased the duty on all three salts to 1½ cents a pound.

The determined efforts on the part of European exporters to capture the whole of the United States market for chlorates led to the closing of the National Electrolytic plant in 1921 and the North American Chemical Company plant in 1926,

leaving Oldbury Electro-Chemical Company the only manufacturer of chlorate (sodium chlorate) on the North American continent. In spite of this vigorous European competition, Oldbury Electro-Chemical Company continued the manufacture uninterruptedly and also continued to manufacture potassium perchlorate. The entire amount of potassium chlorate consumed in the United States from 1926 to 1933 came from Europe.

The experience of Canada in this respect was the same. In 1913–1914 a plant for the manufacture of potassium chlorate similar to that of Oldbury Electro-Chemical Company for sodium chlorate had been built at the Electric Reduction Company (now the Electric Reduction Company of Canada, Ltd.), Buckingham, Quebec, another associate company of Albright & Wilson Limited, of England. During the war this plant was expanded for the production of sodium chlorate, but neither production survived postwar European competition.

Sodium chlorate had been used in Europe as a weedkiller for some years prior to World War I, and the development of its use in the United States during the 20's led to a very great increase in consumption, which was largely taken care of by domestic manufacture. For several years prior to World War I imports of sodium chlorate had been practically nothing, with production and consumption approximately 750 tons a year. Production during the war was increased to 1800 tons and, although after the war there was a considerable amount of imported material, steadily increased during the 20's and 30's until, prior to the outbreak of World War II, it had reached 5000 tons a year, due to agricultural use.

In 1933, the increasing restlessness on the continent of Europe and the realization that the United States and Canada were entirely dependent on European manufacture for chlorate of potash determined Oldbury Electro-Chemical Company to commence the manufacture of chlorate of potash in Niagara Falls, New York, and the Electric Reduction Company of Canada to rehabilitate their chlorate plant. Also, realizing the potentialities of the situation, together with the attempt of the Europeans to take advantage of the situation as regards chlorate of potash in the American market, the Diamond Match Company (largest user of potassium chlorate) decided to build a plant in Oswego, New York. The production capacity of these companies was increased during the next few years until in 1940 with the outbreak of the second war, Oldbury Electro-Chemical Company was in a position to take care of over one-half of the consumption in United States, other immediate requirements being taken care of by the production of Diamond Match Company's plant at Oswego and with stocks on hand. New, but minor, uses, notably for beauty treatment, had been developed for potassium chlorate, but the major use continued to be for matches.

The increasing use of sodium chlorate as a herbicide became so important that a study of the economics of its manufacture and distribution and uses was made by the Department of Agriculture in 1936–37.

A very comprehensive report, including the details of a process for the manufacture of chlorate, was submitted to Congress by H. G. Knight, Chief of the Bureau of Chemistry and Soils of the Department of Agriculture, January 1937. An excellent article on electrochemical production of sodium chlorate was published by P. H. Groggins, Senior Chemist, and his associates (2).

Within two years prior to the beginning of World War II both French and German producers were considering the manufacture of chlorate of potash and/or soda in one or the other of our Western states. Before their plans materialized, however, the war started. In 1941, Western Electro Chemical Company commenced manufacture of chlorate of potash on a small scale at Los Angeles, and by the end of 1941 the entire requirements of potash were being manufactured in the United States, and nearly all the requirements of sodium chlorate.

Pennsylvania Salt Manufacturing Company commenced manufacturing of both soda and potash salts in 1942 at Tacoma, and the International Minerals and Chemical Company started the manufacture of potassium chlorate in 1942 at Cincinnati, but closed down shortly after the end of World War II.

Part of the basic magnesium plant built for war purposes by the United States Government at Henderson, Nevada, and closed down before the end of the war, was converted to the manufacture of chlorates and perchlorates and the operation leased to the Western Electro Chemical Company, which at the present time conducts operations in that location for the manufacture of these products.

In 1941, unable to obtain their requirements of potassium perchlorate used in mining explosives and which formerly had been derived partly from domestic manufacture and partly from imports, the Cardox Corporation, primarily interested in potassium perchlorate, built a plant for the manufacture of sodium chlorate and potassium perchlorate at Claremore, Oklahoma, and at the same location a DPC plant for the United States Government of 200 tons a month of perchlorate, which since the war has not been operated.

At the close of World War II yearly production in the United States was as follows: sodium chlorate 15,000 tons; potassium chlorate 10,500 tons; potassium perchlorate 2,000 tons.

New uses developed during and since the war for sodium chlorate for paper bleaching, cotton defoliation, and the manufacture of chlorite, and for potassium perchlorate for plane rocket assists, metallurgy, and other governmental uses have increased production and consumption of these two products. The production of potassium chlorate remains about the same as at the close of the war.

Another development during World War II was the manufacture of ammonium perchlorate from electrolytically produced sodium perchlorate by both Western Electro Chemical Company and the Electric Reduction Company of Canada, Ltd. Both developed the manufacture of the material for war purposes.

In 1950 U. S. A. production of sodium chlorate was 22,000 tons, potassium chlorate 10,000 tons, and potassium perchlorate 4500 tons. The figure for sodium chlorate and potassium perchlorate will be considerably higher in 1952.

The plant of the Diamond Match Company, at Oswego, New York, has been closed down since the end of the war. They have been able to obtain their chlorate from other producers more advantageously.

At the present moment there are in the United States four manufacturers operating electrolytic processes for the manufacture of either one or all of the chlorates and perchlorates: Western Electro Chemical Company, Cardox Corporation, Pennsylvania Salt Manufacturing Company, and Oldbury Electro-Chemical Company. There is one in Canada—Electric Reduction Company of Canada, Ltd.

REFERENCES

1. Williams Haynes, "*A History of the American Chemical Industry*," Vol. IV, 1923–1929, p. 130, D. Van Nostrand Co., Inc., New York (1948).
2. P. H. Groggins & Associates, *Chem. Met. Eng.*, **44**, 302 (1937); **45**, 691 (1938).

A History of the Hydrogen Peroxide Industry

M. E. Bretschger and Edward Shanley[1]

Hydrogen peroxide was discovered in 1818 by the French chemist Thenard. His preparations were made by reacting barium peroxide with acids. Little or no use of this discovery was made for over 50 years. In 1866 the French chemist Tesse De Motay is said to have suggested the use of hydrogen peroxide as a bleaching agent. By this time chlorine had been in general use for textile bleaching for over 60 years.

The first commercial manufacturing of hydrogen peroxide seems to have been carried out by the barium process at the plant of Schering in Berlin starting in 1873. Following this, hydrogen peroxide came into use for pharmaceutical purposes and for the bleaching of straw and silk, as well as for certain cotton, wool, and rayon specialties. Some bleacheries operated small scale plants for the conversion of barium peroxide to hydrogen peroxide.

The electrolytic method for making hydrogen peroxide may be traced back to the research of Faraday who observed in 1832 that sulfate solutions could be oxidized at a platinum anode. After many years of effort on the part of Brodie, Berthelot, Traube, and others, the products of this oxidation were found to be the anions (SO_5^-) or ($S_2O_8^-$) depending upon the conditions. Marshall isolated the potassium salt $K_2S_2O_8$, commonly called potassium persulfate, in 1891.

Teichner, working at the Consortium fur Elektrochemische Industrie in 1905 first proposed the idea of manufacturing hydrogen peroxide by hydrolysis of persulfates and subsequent recovery of the peroxide by distillation. About 1910 the Osterreichische Chemische Werke in Weissenstein set up the first commercial plant for this purpose. Sulfuric acid was oxidized to $H_2S_2O_8$ on platinum anodes, after which hydrogen peroxide was recovered as proposed by Teichner. This process was a commercial success and is still operated on a large scale.

In 1909, the German chemists Pietzsch and Adolph obtained a patent on an alternative way to synthesize hydrogen peroxide via electrolytic persulfate. This process, operated since 1912 by the Elektrochemische Werke Munchen, consists of anodically oxidizing an ammonium bisulfate solution to yield ammonium persulfate. This oxidation can be carried out at very high current yields. The ammonium persulfate solution is treated with potassium bisulfate whereby the sparingly soluble potassium persulfate separates out. This salt is mixed with 50°Be sulfuric acid and heated under vacuum, whereby hydrogen peroxide is formed and immediately distilled from the reaction mixture. Because of the recrystallization step this process is capable of making exceptionally pure and stable hydrogen peroxide. It was the basis for much of the German supply during both World Wars.

The Riedel and Lowenstein process for making hydrogen peroxide combines the high current yields of ammonium bisulfate electrolysis with the convenience of all-liquid operation, the ammonium persulfate solution being taken directly from the electrolysis to the hydrolysis and distillation stage. This process, first used by J. D. Riedel E. De Haen A. G. is also exploited on a large scale at the present time.

Hydrogen peroxide from the various electrolytic processes proved to be purer and more stable than that from the barium process, and in addition was readily prepared at higher concentrations, such as 27.5 per cent, 35 per cent, and 50 per cent. As a result of these factors the electrolytic processes quickly attained a dominating position in peroxide manufacture.

Electrolytic hydrogen peroxide was first made in the U.S.A. in 1926. Since that time American producers have made great strides in improving the product, its shipping containers, and the manufacturing processes. Regarding the product, the most important improvements have been in the storage stability. Hydrogen peroxide solutions tend to break down into water and oxygen, a process which is accelerated by most metals, almost all impurities such as heavy metal ions, dust and dirt, and many other materials. The work of Reichert and collaborators exemplifies successful research into means for improving the stability of commercial hydrogen peroxide. In a series of patents issued during the 1930's and assigned to the Du Pont Company, these men disclosed the tin process for peroxide stabilization, furnishing one means for making commercial hydrogen peroxide so stable that only one or two per cent of the active oxygen is lost during 24 hours at 100°C

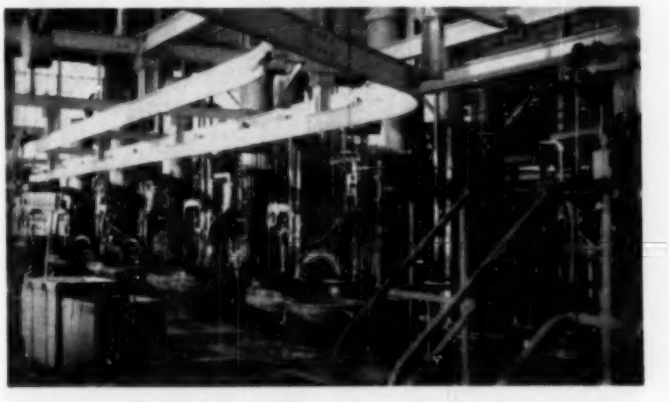


FIG. 1. Early batch-type distillation

and less than this amount in a year of normal storage. Similarly and subsequent to the above, many other stabilizing reagents have been developed and particularly has the development of processes for very high purity peroxide furthered such program.

Hydrogen peroxide was originally shipped only in glass bottles and carboys. In 1931 the Buffalo Electro-Chemical Company pioneered the use of aluminum tank cars for shipping concentrated hydrogen peroxide. Suitable aluminum drums were developed a little later and today almost all peroxide shipments are made in one or another of these containers. Aluminum storage tanks are also commonly employed at the point of use. The peroxide industry could not have reached its present size without the development of these safe, inexpensive and convenient shipping and storage containers.

Great strides have also been made in manufacturing operations. Modern peroxide stills have about eight times the throughput of the original European counterparts. Fig. 1 and 2 show the contrast between the older batch-type distillation and a modern still room. Fig. 3 shows a modern battery room, the cells of which are operated at about three times the current input of early models.

Improvements in peroxide technology are also apparent in the range of available concentrations of peroxide. The standard commercial concentration was 27.5 per cent H_2O_2

[1] Buffalo Electro-Chemical Company, Inc., Division of Food Machinery and Chemical Corporation, Buffalo, New York.

in the 1930's. Today most deliveries are made at 35 per cent or 50 per cent, and 90 per cent H_2O_2 is readily available.

Perhaps the most tangible evidence for improvement in manufacturing methods is furnished by price comparisons. In a time of rapid inflation the price of hydrogen peroxide has shown a downward trend as illustrated in Fig. 4. This record has been achieved by continual refinements in processing, permitting a steady reduction in costs.

FIG. 2. A modern peroxide still room

FIG. 3. A modern battery room

Following the introduction of the electrolytic hydrogen peroxide into the U.S.A., large-scale application research was undertaken in this country. From 1925 to the present time American peroxide producers have invested a total of about 1000 man years in such research. The industrial applications of the product have followed a sharply rising curve, due in large measure to this factor. The growth curve is illustrated in Fig. 5. A few of the important uses, most of which were fostered and developed in large part by the hydrogen peroxide industry, are outlined below.

An early use for hydrogen peroxide was in the bleaching of cotton goods, and by the early 1930's hydrogen peroxide was being used for specialty bleaching in several American cotton mills. The original impetus was furnished by the fact that cotton goods containing vat-dyed portions could be peroxide bleached without damage to the colors. The reliability and safety of the peroxide bleaching process, and the excellence of the results led to a great swing toward the use of this re

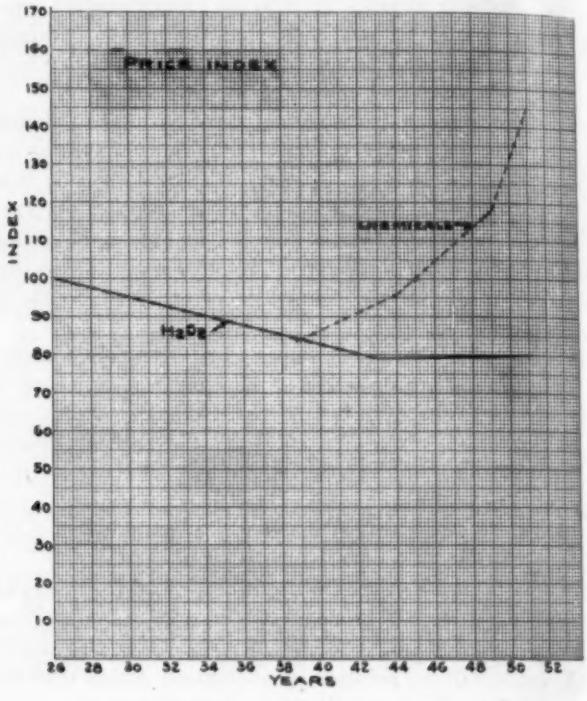


FIG. 4. Price of hydrogen peroxide

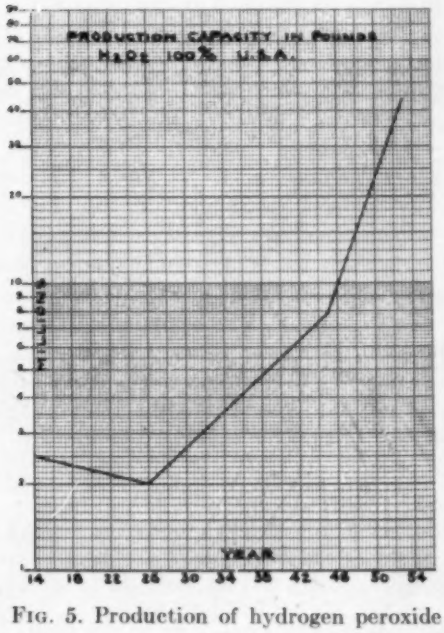


FIG. 5. Production of hydrogen peroxide

agent in all cotton processing. During the 1930's this trend carried hydrogen peroxide into the bleaching of all types of cotton yarns, knit goods, and woven goods, both colored and all white. The continuous bleaching system for use in processing cotton piece goods appeared in 1940. Having the usual merits of continuous operations, such as faster processing, greater uniformity, and low cost, this process was an immediate success. Its adoption was delayed by material shortages during the war years, but by 1948 most large scale cotton piece

goods bleaching in the U.S. was being carried out in continuous peroxide equipment. In addition, the process has been adopted by many bleacheries abroad, and continuous peroxide bleaching equipment is now coming into use all over the world.

About 80 per cent of all cotton bleaching in the U.S. is now carried out with hydrogen peroxide, and this for some years was the largest single use for H_2O_2.

The bleaching of wool with hydrogen peroxide has been practiced, at least on a small scale, for a great many years. However, until the early 1920's peroxide wool bleaching was a specialty operation in the U.S. With the availability of domestic hydrogen peroxide, wool bleachers have turned increasingly to the use of this chemical in place of the various reducing bleaches. Starting in 1928, hydrogen peroxide processing was adapted to the continuous wool scouring machine. Since that time peroxide bleaching has been applied to a constantly increasing proportion of the wool produced in this country.

The bleaching of groundwood pulp has become a major outlet for peroxide during the past few years. Interest in peroxide for this purpose was fostered by the desire to use groundwood pulp as a partial replacement for chemical pulp in book and magazine papers. Groundwood pulping yields approach 100 per cent based on the wood, while chemical pulping by its very nature discards about half the wood weight, retaining only the cellulose for paper making. However, groundwood pulp is dark in color and is not bleachable by standard chlorine pulp bleaching techniques. The development of peroxide bleaching methods for groundwood pulps has fostered the use of this cheaper pulp on a very large scale, and most nationally circulated magazines are currently printed on groundwood content paper.

The newest big use for peroxygen chemicals is in the field of organic synthesis. The current availability of concentrated hydrogen peroxide makes it convenient and economical to synthesize performic, peracetic, and other peracids. This in turn makes it possible to carry out numerous organic oxidation reactions. Examples are the synthesis of epoxy and hydroxy stearic acids from oleic acid. The epoxy compounds are especially valuable as stabilizers and plasticizers for chlorinated polymers and for the production of new resins and surface active materials. Other valuable new reactions of the same type include the synthesis of an epoxidized insecticide, Dieldrin, and the preparation of 17 hydroxy stearoids, such as cortisone.

Drug and cosmetic uses, longtime standby of the peroxide industry, continue to thrive, although now constituting a minor part of total peroxide consumption. Some millions of small bottles of hydrogen peroxide are sold annually for use in hair dyeing, hair bleaching, in cold waving, and for various pharmaceutical uses. Most of this material is bottled at 3 per cent or 6 per cent H_2O_2 by firms purchasing 35 per cent in bulk containers.

Before World War II the Germans carried on secret large-scale developments looking toward the production of very highly concentrated hydrogen peroxide and its use in weapons of war. Large facilities were set up for making 80–85 per cent hydrogen peroxide. As it turned out, these developments were not completed in time to have a decisive effect. Some, like the high speed submarine and the long range rocket might have changed the course of the war.

The American peroxide industry, when appraised of the need, was able to outdo European practice. In record time the Armed Forces were provided with a supply of 90 per cent hydrogen peroxide, purer and more concentrated than that available in Germany. The military research conducted on the basis of this material is largely under security restrictions, but it is safe to assume that our country will not lag in the exploitation of this compact and extremely powerful energy source.

To supply the expanding demands outlined above has required continuous expansion of the hydrogen peroxide producing facilities. Hydrogen peroxide has been in very tight supply in this country many times in the past ten years, yet essential demands have always been met. Because of the inevitable lag between a decision to expand and the completion of a plant, continued approximate balance of supply and demand is evidence of foresight on the part of management. At the present time and for the immediate future it is indicated that all demands for this chemical can be fully met.

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Feature Section

AUGUSTUS JAMES ROGERS

Pioneer American Electrometallurgist

Otto L. Kowalke[1]

In this 50th year since the founding of The Electrochemical Society, it is justifiable to recount and record the electrometallurgical researches and achievements of Augustus James Rogers who joined the Society on February 3, 1903. He was a teacher in the high schools of Milwaukee, Wisconsin, from 1875 until he died in 1907. In addition to his teaching duties he did researches in the electrometallurgy of sodium and of aluminum, obtained patents, served as expert witness in patent litigation, and wrote essays for engineering magazines and for scientific societies. That is an exceptional record for a high school teacher, whether it be measured with the standards of seventy years ago or even with those of today.

Education and Teaching Career

Augustus James Rogers was born at Cape Vincent, New York, on February 18, 1848. He was graduated from the high school at Watertown, New York, and from Cornell University, Ithaca, New York, in 1871, with the degree of Bachelor of Philosophy. During the school year 1873–74, he studied physics, calculus, and experimental chemistry at Heidelberg University, Germany, where he had Professors Bunsen and Kirchhoff as teachers. The following year, 1874–75, at Frederick William University in Berlin, he studied experimental physics under Professor Helmholtz.

In September 1875 Rogers went to the East Division High School in Milwaukee, Wisconsin, as a teacher of physics and chemistry. He was promoted to vice-principal in 1888, and to principal in 1892. Then from 1901 until his death in 1907, he taught physics and chemistry in the South Division High School of Milwaukee.

Experiments in Electrometallurgy, 1875 to 1886

Rogers began his experiments shortly after beginning his work as a teacher. The equipment in his laboratory was rather meager for his purposes. To measure electric current, he had to make and use voltameters of silver and of copper. But because they took so much time and effort, he made a tangent galvanometer with which he could measure the amperes with an accuracy adequate for the purpose.

In this period, batteries were the only sources of electric current. The first company to sell electricity was the Badger Electric Illuminating Company, incorporated in July 1885. Rogers reports that in 1878 he bought a 50-cell Ladd-Grove battery from George Wale of Stevens Institute of Technology. The new 50-cell battery made it possible to do experiments that required fairly large currents and at voltages higher than previously obtainable.

[1] Chemical Engineering Department, University of Wisconsin, Madison, Wisconsin.

Lacking crucibles, Rogers used clay pipes instead, the kind commonly used by men for smoking tobacco. An iron wire was pushed through the hole in the stem and into the bottom of the bowl of the pipe to serve as the cathode; the anode was a carbon rod inserted into the bowl from the top. Such an assembly was then heated in a Bunsen flame until the charge of sodium chloride was melted, whereupon the current was turned on. Because the iron wire was faulty as a cathode, Rogers put either lead or tin in the bottom of the bowl, which, when melted, would serve as the cathode. The iron wire then was only a conductor. The molten lead and tin, moreover, formed alloys with the sodium liberated by electrolysis. Such were the conditions and procedures in the experiments by 1879. John F. Burke, once a teacher in another school, later a lawyer, and long a close friend, tells of those early experiments and also of Rogers' attempts to win sodium and aluminum by electrolysis.

The crucible problem was solved when, in 1881, a Mr. Kendrick, who had an abstract of title and law business, gave some help. He bought crucibles and also had some made by the potter of the local glass factory in accordance with Rogers' specifications. These crucibles were around 3 in. in diameter by 4 to 5 in. high, and of various shapes.

Because the crucibles needed more heat than could be obtained with a Bunsen flame, a charcoal furnace was borrowed. In it, some Battersea crucibles, lined with alumina, were heated from below. The anodes were carbon rods inserted into the crucibles from the top, and the cathodes were either molten lead or tin to which connection was made by an iron wire incased in clay and also inserted from the top. In some later experiments an iron rod was passed through a hole in the bottom of the crucible and held in place with lock nuts inside and outside so that it was in contact with the molten cathode. The crucibles were heated from below. The electrolysis of fused sodium chloride, using a molten lead cathode, gave a lead-sodium alloy which was judged to be homogeneous. Metallic sodium was obtained only when an iron wire alone was made the cathode. With such equipment Rogers tried, in 1882, to get metallic aluminum by electrolyzing fused "potash alum."

The first patent.—The successes in the experiments and the encouragement of friends prompted Rogers, in April 1883, to apply for a patent on a "Process of Getting Difficultly Reducible Metals by Electrolysis." Patent 296,357 was granted on April 8, 1884 and assigned two-thirds to Henry Mann and Julius Koebig.

The ill-fated pilot plant.—The facilities for experimentation, either at the high school laboratory or at Rogers' home, were quite limited. A small plant in which experiments could be done on a larger scale would have been most desirable

but that required money. In the autumn of 1883, Henry Mann, a neighbor of Rogers and a manufacturer in Milwaukee, bought the interest of Kendrick. In December 1883, Mann purchased a dynamo, giving 10 amperes at 60 volts, and installed it in a building he owned in the Bay View section of Milwaukee. Julius Koebig, an associate of Mann, got the plant ready for operation. In January 1884, on the first test run, with Koebig in charge and Rogers absent, the crucibles got overheated and broke and the dynamo was burned out. Thereafter, all experiments at that plant were abandoned. Rogers again had to rely on batteries for electricity.

The first trials to electrolyze fused mixtures of sodium chloride and cryolite were made in April 1884. The range of the compositions of the electrolytes was from one part each of salt and of cryolite to two parts of salt and one of cryolite. The crucibles used were of clay, the electrodes were like those described previously, and the cathode was molten tin. The aluminum obtained was in globules about the size of a pea or bean. The quality of the product was estimated by making measurements of the specific gravity of the globules.

In 1884 certain quantitative measurements were made respecting the amount of metal deposited by electrolysis at the cathode. For these tests a Grove battery furnished the electricity, Battersea crucibles held the fused sodium chloride, and "the carbon anode and the iron wire cathode terminating in a tube of lime, dipped into the molten salt. As soon as metallic sodium was seen to escape and burn at the surface of the liquid, the current was stopped, the liquid cooled, the crucible broken, and the amount of sodium determined by a standard acid solution. Some of the sodium was oxidized, but a considerable amount would be found in the tube in the pure metallic state."

Experiment	Amp	Time in sec	Observed sodium	Theoretical sodium
			g	g
No. 1	3.2	90	0.04	0.066
No. 2	2.5	480	0.04	0.286
No. 3	2.8	360	0.16	0.24

Near the end of the year 1886, Rogers tried to electrolyze a fused mixture of alumina (Al_2O_3) in potassium cyanide in a glass U tube. In the bottom of the U he had molten tin for the cathode. That was connected to the circuit by an incased iron wire that came down one leg of the U; a carbon rod anode came into the other leg. The potassium cyanide was fused and then the alumina added. For this test he used alumina for the first time. The results of this test are not recorded.

Experiments from 1886 to 1890

Until about 1886, Rogers did most of his experimenting in the school laboratory and in his home. By judicious disclosures of the aims and the results of his experiments, he won the interest and assistance of several influential men of Milwaukee. That marked the beginning of the second period of experimentation.

The organization of the American Aluminum Company in August 1887 "was due largely to D. J. Whittemore," then Chief Engineer of the Chicago, Milwaukee, and St. Paul Railroad; Henry Mann was made its president. The company was formed "for the purpose of manufacturing and use of aluminum and other difficultly reducible metals including sodium, potassium, and magnesium. The method by which it was proposed to obtain these metals is by electrolysis of their fused salts."

Rogers believed that he could also make pure alloys of any metal that would unite with aluminum. In December 1892 he exhibited such an alloy, made in 1886, when testifying in the patent interference No. 14039 of Lossier vs. Rogers vs. Cowles and Cowles vs. others.

Upon the suggestion of Rogers, the directors decided to build an experimental plant, corresponding to the "pilot plant" of today, in which to test out ideas further. By Christmas 1887, the 20 by 28 ft-pilot plant, at the rear of Rogers' home, was completed and the furnaces installed. Rogers spent the 1887 Christmas vacation trying to get an old Brush dynamo and a Fuller dynamo to work, but was unsuccessful. A new dynamo arrived on January 22, 1888; it was rated at 4000 watts and to deliver 100 amperes at 40 volts. The new dynamo, together with the 10 hp Otto gas engine gave reliable electric energy.

The pilot plant period, 1887 to 1889.—In the beginning, breakage of crucibles was extensive. Consequently, the furnace was rebuilt so that the crucibles rested on a pier of fire-brick allowing the flames to pass over and around the crucibles. That arrangement not only reduced the breakage, but it also permitted the iron connections to the molten cathodes to come up through the pier and into the bottoms of the crucibles.

In the first report to the directors of the company in 1888, Rogers tells of his disappointment over not being able to get help that had the required skills. He tells of working at the plant at night, on Saturdays and Sundays, and during vacations, and that he made all the chemical analyses of the products of electrolysis. Cryolite, he said, was the most expensive of all the raw materials bought, and the small amounts obtained cost 6½ cents a pound, or at the rate of $125 per ton. Aluminum, he reported, was selling for $7 per pound, wholesale, and he estimated that it could be made for $2.50 per pound and sold for $4.00.

Among other things reported to the directors in 1888 and 1889, Rogers included detailed accounts of certain experiments. In the experiments selected by the author for this essay, the electrolyte in all cases was a fused mixture of sodium chloride and cryolite.

"On February 28, 1888, the first Al was made in appreciable quantities by electrolysis, using a clay crucible with an iron electrode in the bottom and carbon in the top, using cryolite and salt as electrolyte. I ran with 20 volts and 80 amperes for 2¾ hours and collected 6 grams of aluminum, a considerable amount of pure sodium, and a large amount of sodium oxide."

During April and May 1888, he experimented with various molten cathodes, such as lead, tin, antimony, bismuth, zinc, and cadmium. He decided in favor of lead, because it did not alloy with aluminum, but did alloy with sodium. The sodium would then replace all the aluminum from the cryolite and there would be no loss of sodium or aluminum.

On August 15, 1888, using four pots in series, he passed 80 amperes at 33 volts through them for 7¾ hours. The yield was nearly ¾ lb of aluminum and in addition there was an equivalent of ¼ lb more obtainable by the sodium that remained in the pots.

The last experiment in 1888 was made on August 23. There were 4 pots in series, through which 75 amperes at 36 volts were passed for 7 hours. The yield was only 6 oz of aluminum because one of the pots sprang a leak so that nearly half of the power was wasted. From that date until the end of 1888, time and effort were spent in making repairs and alterations.

From December 1887 to about September 1888 around 12 to 15 pounds of aluminum, in all, were made. The company made no solicitations for orders, no attempts to fill unsolicited orders nor to sell any of its product. Sample bars, however, were sent to Tiffany and Company of New York and also to a company manufacturing dental plates that wanted to try the metal for artificial teeth Some of those sample bars weighed as much as ½ lb.

After September 1888, work in the pilot plant was done but infrequently. The directors believed that the experiments had shown what could be accomplished, but decided to wait upon the outcome of two applications for patents before spending more money. One of these applications, No. 252,199, for "Reduction of Metals by Electrolysis," was filed October 13, 1887, and was finally denied on August 20, 1888. The other application, No. 278,573, for a "Process of Obtaining Difficultly Reducible Metals and Their Alloys from the Salts of Such Metals," was filed June 29, 1888. There were 43 letters and replies between the Patent Office and Rogers and his attorneys. Then, nearly eight years later, on February 29, 1896, the application was finally rejected and denied.

In a test made July 17, 1889, when 73 amperes at 40 volts were passed for four hours through four pots, a yield of 200 grams (about 7.1 oz) of aluminum was achieved. Of this test Rogers reported to the directors: "That yield is about six times the amount that has ever been obtained by electrolysis, so far as I know. If results as good as that have ever been obtained, they have never been published."

The slackening in the experimental work may have been increased, because Rogers, having been promoted in 1888 to vice-principal of the school, now had to spend more time at school on administrative duties than he did before.

According to his testimony in the lawsuit of the Electric Smelting and Aluminum Company vs. Pittsburgh Reduction Company, Rogers continued his studies in electrolysis until at least 1899. But there is no record at hand concerning the nature of those studies, excepting for the period from February 1891 to June 1891. The experiments there described dealt with the electrolysis of fused mixtures of sodium chloride plus cryolite, cryolite plus alumina, borax plus alumina, and sodium carbonate plus alumina.

Recognition of Achievements

The achievements of Rogers in the electrometallurgy of aluminum and of sodium won him citations in publications, requests for his services as expert witness, and friendly correspondence with scientists respecting technical matters.

Citations in Publications

Joseph W. Richards, in his book, "Aluminium," 2nd ed., 1890, on pages 181–183, tells of Rogers' electrolysis of fused sodium chloride to get sodium, and also of adding cryolite to such fused mass to get aluminum. On pages 280–283, the incorporation, in 1887, of the American Aluminum Company of Milwaukee is mentioned. Rogers found that a paste of alumina, well fired on, was the best lining for the clay crucibles he used. Of the metallic aluminum, Richards says: "A sample of aluminum sent me recently is of very fair quality."

W. Borchers in "Electric Smelting and Refining," 1897, translation by W. G. McMillan of "Elektro-metallurgie," 2nd ed., on page 71, quotes from Rogers' paper before the Wisconsin Natural History Society, April 1889: "In the last three years I have experimented on the reduction of sodium chloride using molten negative electrodes and especially lead." Also on page 128 he writes: "Richards ("Aluminium," 4th ed., 1890) describes an unpatented process of Rogers which aims at electrolyzing melted cryolite with a cathode of molten lead. Here an alloy of lead and sodium is used initially and this separates the aluminum at the expense of the sodium."

C. F. Carrier in "Electrochemical and Metallurgical Industry," Vol. 4, p. 444, November 1906, subtitle "Electrolysis of Fused Sodium Chloride" writes: "The pioneer American worker in this field was A. J. Rogers. His apparatus was an elaboration of the same general features as are involved in the apparatus of Watt and was no more successful. The chief distinction was that Rogers introduced the salt into the electrolytic cell in the molten state." (A. J. Rogers, U. S. Pat. 296,357, April 8, 1884).

Expert Witness in Patent Litigation

(*A*) Butz Thermo-Electric Regulator Company vs. Jacobs Electric Company (Defendant) in U. S. Circuit Court for Eastern Wisconsin, 1888.

(*B*) U. S. Patent Office. Interference No. 14039; Obtaining Aluminium Bronze; Lossier vs. Willson vs. Cowles and Cowles vs. Rogers, *et al*. November 1892. In this case Rogers testified in his own behalf.

(*C*) The Electric Smelting and Aluminum Company vs. The Pittsburgh Reduction Company (Defendant) in U. S. District Court, Northern District of New York, 1899. The record of "Complainants Rebuttal Evidence" fills 1190 pages and shows that 17 witnesses appeared. The testimony of three witnesses: Alfred H. Cowles, President, Electric Smelting and Aluminum Company; Henry Morton, President of Stevens Institute of Technology; and Augustus J. Rogers, Principal of Milwaukee East Side High School, comprises 73 per cent of the 1190 pages. Of this, Rogers' share was about 12 per cent; Morton's 20 per cent; and Cowles' 41 per cent.

The questions asked Rogers on direct and on cross examination showed him to be well informed. Prominent among the questions were: (*a*) relation of current density in electrolysis to output of metal, (*b*) meaning of "secondary reactions," (*c*) is alumina an electrolyte, (*d*) principle of minimum expenditure of energy, (*e*) latent heat of fusion, liquefaction, and of specific heat, and (*f*) the nature or kind of solutions used to deposit copper, silver, and brass.

Correspondence with Prominent Scientists

(*A*) Joseph W. Richards, of Lehigh University, when writing the 2nd edition of his book, "Aluminium," asked Rogers, on July 3, 1889, for more information on his process. He also acknowledged the receipt of a small bar of metallic aluminum and said: "Yours is one of the two processes which make pure aluminium, now in use in the United States; the other is an electrolytic one in Pittsburgh."

On July 24, Rogers sent Richards a piece of aluminum foil. Richards replied that the foil may contain some lead. He also believed that the lead-sodium alloy would react with the fused bath containing cryolite and thus increase the yield of aluminum.

In October 1889, Richards acknowledged the calculations made by Rogers on the actual output in electrolysis as compared with the theoretical, and also told that he had been working on the same problems.

(*B*) George Gore, F.R.S., of the Institute of Scientific Research in Birmingham, England, corresponded with Rogers from 1887 to 1889 respecting developments in electrometallurgy in England and in the United States, particularly with respect to aluminum and copper.

Patents

Rogers obtained two U. S. Patents: No. 296,357, on April 8, 1884, for a "Process of and Apparatus For Reducing Metals by Electrolysis," and No. 469,454, on February 23, 1892, for a "Process of and Apparatus For Controlling Discharge of Molten Contents of Crucibles and Other Vessels."

Publications

Besides his full-time job as teacher and his extracurricular work in experimental research, Rogers also found time to write essays to be read before scientific societies or printed in engineering magazines. The following is a list of such essays and articles.

Year	*Article*
1885	American Association for Advancement of Science. Ann Arbor Meeting. "Electrolysis of the Salts of Alkalis and Alkaline Earths."
1887	"Syllabus of Laboratory Work in Chemistry." Published by Authority of the School Board of Milwaukee, Wisconsin.
1889	Wisconsin Natural History Society (April). "Experimental Researches in the Reduction of the Difficultly Reducible Metals."
1891	*Amateur Electrician*, Vol. I (April, May, June, July). "Galvanic Batteries."
1894	*Electrical Engineering*, Vol. III (June). "Electrolytic Methods." (A paper read before the electrical engineering students at the University of Wisconsin on April 27, 1894).
1895	*Electrical Engineering*, Vol. V (June). "Extraction of Gold by Electrolysis."
1896	*Electrical Engineering*, Vol. VII (May). "Helmholtz [illegible] (An address given in Milwaukee in the East Divisio[illegible] High School Lecture Course.)
1901	Wisconsin Academy of Sciences, Arts and Letter[illegible] (December). "Note on the Use of the Terms 'Flux' an[illegible] 'Solvent.' "

Acknowledgments

Grateful acknowledgment is hereby made to the followin[illegible] persons for help in getting information about various matter[illegible] in this narrative:

To Augustus J. Rogers, Jr., of Traverse City, Michigan[illegible] for permission to inspect and read numerous documents[illegible] letters, and records that belonged to his father.

To Oliver W. Storey, Chicago, Illinois, for the information[illegible] that, among the papers left by the late Professor Charles F[illegible] Burgess, he found a letter written by Mrs. Augustus J. Rogers[illegible] Sr., in October 1909. In this letter Mrs. Rogers told that she[illegible] was giving certain papers, documents, and apparatus, belong[illegible] ing to her husband, to the Chemical Engineering Department[illegible] of the University of Wisconsin. Professor Burgess was then the[illegible] Chairman of that department.

To Mrs. Rogers, Sr., for her gift to the University. That[illegible] material is still in the museum of the Department and it was[illegible] the source of most of the information on matters revealed in[illegible] this essay.

Sustaining Members of The Electrochemical Society

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American Platinum Works, Newark, N. J.

American Potash & Chemical Corp., Los Angeles, Calif.

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Armour Research Foundation, Chicago, Ill.

Atlas Powder Company, Wilmington, Del.

Auto City Plating Company Foundation, Detroit, Mich.

Bell Telephone Laboratories, New York, N. Y.

Bethlehem Steel Company, Bethlehem, Pa.

Buffalo Electro-Chemical Company, Buffalo, N. Y.

Burgess Battery Company, Freeport, Ill.

Canadian Industries Limited, Montreal, Canada

Chrysler Corporation, Detroit, Mich.

Columbia-Southern Chemical Corporation, Pittsburgh, Pa.

Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

Crane Company, Chicago, Ill.

Diamond Alkali Company, Pittsburgh, Pa.

Dow Chemical Company, Midland, Mich.

E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

E. I. du Pont de Nemours & Company, Screen Division, Towanda, Pa.

Eagle-Picher Company, Joplin, Mo.

Eaton Manufacturing Company, Stamping Div., Cleveland, Ohio

Electric Auto-Lite Company, Toledo, Ohio

Electric Storage Battery Company, Philadelphia, Pa.

The Eppley Laboratory, Newport, R. I.

General Chemical Division, Allied Chemical & Dye Corporation, New York, N. Y.

General Electric Company, Schenectady, N. Y.

Gould-National Batteries Inc. Depew, N. Y.

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Great Lakes Carbon Corporation, Niagara Falls, N. Y.

Hanson-Van Winkle-Munning Company, Matawan, N. J.

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Hooker Electrochemical Company, Niagara Falls, N. Y.

Houdaille-Hershey Corporation, Detroit, Mich.

International Graphite & Electrode Corporation, St. Marys, Pa.

International Minerals & Chemical Corporation, Chicago, Ill.

International Nickel Company, New York, N. Y.

Kaiser Aluminum & Chemical Corp., Division of Metallurgical Research, Spokane, Wash.

Mathieson Chemical Corporation, Niagara Falls, N. Y.

McGean Chemical Company, Cleveland, Ohio

Metal & Thermit Corporation, New York, N. Y.

Monsanto Chemical Company, St. Louis, Mo.

National Carbon Division, Union Carbide and Carbon Corporation, New York, N. Y.

National Cash Register Company, Dayton, Ohio

National Research Corporation, Cambridge, Mass.

Niagara Alkali Company, Niagara Falls, N. Y.

Norton Company, Worcester, Mass.

Pennsylvania Salt Manufacturing Company, Philadelphia, Pa.

Potash Company of America, Carlsbad, N. Mex.

Promat Division, Poor & Company, Waukegan, Ill.

Solvay Process Division, Allied Chemical & Dye. Corporation, Syracuse, N. Y.

Stackpole Carbon Company, St. Marys, Pa.

Standard Steel Spring Company, Coraopolis, Pa.

Stauffer Chemical Company, San Francisco, Calif.

Sylvania Electric Products, Inc., Bayside, N. Y.

Tennessee Products & Chemical Corporation, Nashville, Tenn

Udylite Corporation, Detroit, Mich.

Union Carbide Company, Electrometallurgical Division, New York, N. Y.

United Chromium, Inc., New York, N. Y.

Vanadium Corporation of America, New York, N. Y.

Victor Chemical Works, Mt. Pleasant, Tenn.

Wagner Brothers, Inc., Detroit, Mich.

Western Electric Company, Inc., Chicago, Ill.

Western Electrochemical Company, Los Angeles, Calif.

Westinghouse Electric Corporation, E. Pittsburgh, Pa.

Westvaco Chemical Division, Food Machinery and Chemical Corporation, New York, N. Y.

Willard Storage Battery Company, Cleveland, Ohio

Wyandotte Chemicals Corporation, Wyandotte, Mich.

Current Affairs

Candidates for Office—1953-1954

ROBERT J. MCKAY

Robert J. McKay

Presidential Candidate

Robert J. McKay has been a vice-president of the Society for the past three years, and has previously served as Chairman of the New York Section, Chairman of the Corrosion Division, and in various other capacities.

Mr. McKay was born in Washington County, New York, in 1887. He received his B.A. degree at Butler College in 1910 and while there was assistant to Dr. R. B. Moore who was beginning his work on radioactivity and atomic fission. His B.S. degree, in physical chemistry, was received from the University of California in 1913, at which time he was an instructor at this university. After early work with western smelters, he joined the International Nickel Company in 1916. Following experimental work which led to the use of *p*H control in nickel refining, he did work at Mellon Institute on corrosion of nickel alloys for the International Nickel Company. Later, as the company's Superintendent of Technical Service he was active in the development of new products, such as nickel clad steel and the alloy, Inconel, which has had recent attention in connection with jet and other high temperature engines—and he was author of the first paper describing the properties of Inconel. Since 1938 Mr. McKay has been Chemical Engineer in charge of Plating Sales and Development and, more recently, he has been interested in new industrial uses involving corrosion, heat resistance, and mechanical strength as contrasted with the more commonly known decorative uses of nickel plating.

Mr. McKay's publications include some forty technical papers on the corrosion properties of nickel alloys, many of them in the TRANSACTIONS of the Society. He is co-author of the American Chemical Society Monograph on "Corrosion Resistance of Metals and Alloys."

As an officer of the Society, Mr. McKay has been a constant attendant at Society and Board meetings and has favored the policy of the improved Journal and an advertising program to support it.

Jerome Strauss

Vice-Presidential Candidate

Jerome Strauss, vice-president and technical director of Vanadium Corporation of America, New York City, was born in New York in 1893. He received his M.E. degree from Stevens Institute of Technology in 1913. In the same year he joined the metallurgical department of Illinois Steel Company and, later, Western Drop Forge Company, as chemist and metallurgist. During World War I Mr. Strauss served as a Lieutenant in the Ordnance Department, U. S. Army, and from 1919 to 1928 he was materials engineer at the U. S. Naval Gun Factory. In 1928 he joined the Vanadium Corporation of America as chief research engineer, becoming vice-president in charge of research and development in 1935, and technical director in 1946.

JEROME STRAUSS

Mr. Strauss has published numerous papers on low-alloy and high-alloy steels, including the stainless or corrosion-resistant steels, tool steels, and high-strength bronzes. He holds eight U. S. patents in this and allied fields. He has made a major contribution in the initial use of the low-alloy, high-strength sheet-steels and the new boron steels.

Mr. Strauss joined The Electrochemical Society in 1935 and has participated in the management of its rare metals symposia. He has also been active in other scientific organizations.

Hans Thurnauer

Vice-Presidential Candidate

Hans Thurnauer, vice-president and director of research of American Lava Corporation, Chattanooga, Tennessee, has been a member of The Electrochemical Society since 1935. Born in 1908 in Nuremberg, Germany, he received his engineering degree in chemistry from The Charlottenburg Institute of Technology, Germany, in 1930, and received his M.Sc. degree in ceramic engineering, in this country.

from the University of Illinois in 1931. After returning to Europe, he worked as ceramic research engineer in German and British plants until he made his permanent residence in the United States in 1935. Since that time he has been connected with the American Lava Corporation, manufacturers of technical ceramics.

Mr. Thurnauer served as a member of the Technical Industrial Intelligence Committee, investigating ceramic plants in Germany after the war. He is the

HANS THURNAUER

author of numerous articles on technical ceramics and holds various patents in this field. He has been active in furthering the interests of the Society in the field of technical ceramics both for dielectric and high temperature applications.

International Chemistry Congress in Sweden, 1953

The XIIIth International Congress of Pure and Applied Chemistry will be held in Stockholm from July 29th to August 4th, 1953, and in Uppsala from August 5th to 7th, 1953.

The congress will comprise a Physical Chemistry Section with the following groups: Chemical Thermodynamics and Thermochemistry, Electrochemistry, Surface Chemistry and Colloid Chemistry, Chemical Kinetics, and Other Fields of Physical Chemistry. There will be arranged, also, a Symposium on the Chemistry of Wood and Wood Constituents, with the following groups: Structural Chemistry of Wood Constituents, The Chemistry of Cellulose and Hemicellulose, and The Chemistry of Lignin.

Immediately after the congress in Stockholm, a Symposium on Macromolecules is to be held in Uppsala.

Those who would like to present papers (of a maximum duration of 15 minutes) are cordially invited to do so and application should be made as early as possible. Contributions may be presented in any language but it is felt that those in English, French, or German, and especially those in English, will be most readily understood by the majority of members. For further information and particulars write to "XIIIth International Congress of Pure and Applied Chemistry," Stockholm 70, Sweden.

Scientific Education Aided by Industries

Manufacturing Chemists' Association

Faced with a long-range shortage of trained manpower, the nation's chemical companies recently were asked by the Manufacturing Chemists' Association to launch a drive to get more students into the field. As an initial step in the program, MCA is sending the companies copies of a manual outlining various student guidance activities.

Because of the rapid growth of the chemical industry, Board Chairman William H. Ward stated, there is already a shortage in the number of chemists and chemical engineers available and the increase in students in these fields is far slower than the rate of expansion by the industry.

The object of the drive is to inform high school students, teachers, and parents in every plant community of the career opportunities opening up for qualified young scientists in industrial chemistry and chemical engineering. The manual details a series of suggestions for doing this by plant tours, classroom talks, summer employment, personal interviews, scholarship programs, and other means.

The necessity of increasing the flow of new talent is evident in the disparity between the industry's growth and the number of graduates now coming out of colleges, Mr. Ward said.

Monsanto Chemical Company

Seventeen undergraduate scholarships to be administered by colleges or universities are included in the 1952–53 Monsanto Chemical Company program of aid to scientific education, as announced by Dr. Carroll A. Hochwalt, Monsanto vice-president. Also included in the program are 13 graduate fellowships, one graduate scholarship, and seven grants-in-aid to various schools.

The undergraduate scholarships, which are new to industry, as well as to Monsanto's program this year, have been granted chiefly to chemical engineering schools. They are to be awarded to outstanding seniors on the basis of merit and will be sufficient to cover tuition at the respective schools.

The Monsanto fellowships are the highest form of award, and are expected to have an average value of approximately $3,000, part of which goes to the school while the larger part goes to the fellow. Selection of the individual recipients is done entirely by the schools. Several fellowships or grants-in-aid, not included in this general program, have been established by Monsanto divisions or departments for study in specific fields. Lists of the schools where the scholarships and fellowships are established are obtainable from the company.

Vast Growth Seen in Electronics Renewals

Because of the increasing use of electronics equipment, the nation's electronics distributors have been urged to prepare now to meet an expanding market for renewal electron tubes, component parts, and electronic test equipment that is expected to reach a national sales volume of one billion dollars by 1955, and more than two billion dollars by 1960.

Speaking at the convention of the National Electronics Distributors Association, H. F. Bersche, RCA Victor tube executive, emphasized that distribution of electronic equipment in fields of communications, industry, science, and home entertainment is proceeding at a tremendous rate of growth.

"To meet the renewal requirements of the 'Electronics Age,' " he predicted, "the electronics distributing industry will need, within the next three years, to grow two-thirds larger than it is today and within the next eight years, three and a half times its present size."

Leading the national growth in this market, Mr. Bersche said, are five relatively new electronics developments which will have future and major influence on the renewal sales market. He listed these developments as UHF-Television; microwave relay; industrial television; and eventually transistors and color television.

Weather Research by G-E for Navy

Scientists of the General Electric Research Laboratory, Schenectady, plan to start a one-year study of long-distance weather migrations and cloud physics for the Office of Naval Research, it has been announced.

Dr. Irving Langmuir, Nobel prize winner and consultant for the G-E Research Laboratory, will conduct research into weather movements over long distances. He will extend and intensify studies he has made on the transcontinental travel of weather systems.

The laboratory study of cloud physics will be conducted by Dr. Vincent J. Schaefer, who with Dr. Langmuir discovered methods for producing snow and rain from clouds, and with Raymond E. Falconer, G-E meteorologist. Initially, the study will center around spontaneous formations of ice crystals and the role that atmospheric dust plays in developing snow crystals.

Opens Midwest Office

Arthur D. Little, Inc., Cambridge, Mass., has announced the opening of a Midwest office located at Railway Exchange Building, St. Louis, Missouri. John R. Kirkpatrick will head the new office.

SECTION NEWS

India Section

The India Section of The Electrochemical Society is planning a Symposium on "Electrolytic Alkali-Chlorine" to take place in February 1953. The discussion will include the latest developments in the types of cells, utilization of chlorine, the future of the industry, and related subjects.

* * *

The third number (Volume 1, Number 3, July 1952) of the *Bulletin of the India Section of The Electrochemical Society* has been issued. The *Bulletin* is now published in printed form.

Elsewhere in India

The National Metallurgical Laboratory, Jamshedpur, has arranged to hold a symposium during January 1953 on "Industrial Failures of Engineering Metals and Alloys." It will cover theoretical and practical aspects of service failures.

T. L. Rama Char, *Regional Editor*

Dr. Taylor Elected President of Faraday

Hugh Scott Taylor, dean of the graduate school of Princeton University, was elected president of the Faraday Society for the year 1952–53, at the recent annual meeting of the society held in Cambridge, England.

Dr. Taylor is the first American president of the Faraday Society and also the first president to be chosen from outside Great Britain and Ireland. He is a longtime member of The Electrochemical Society, having joined in 1915.

S. C. Lind Awarded Priestly Medal

Samuel C. Lind, noted nuclear scientist at Oak Ridge, now associated with Carbide and Carbon Chemicals Company, was the recipient of the Priestly Medal, highest award of the American Chemical Society, during the society's annual convention at Atlantic City, September 14–19.

Dr. Lind, a former president of The Electrochemical Society, received the ACS award for "services in chemistry, atomic energy, and as an editor and worker in the society." Following the presentation by Dr. Britton, ACS President, Dr. Lind delivered an acceptance speech reviewing the progress the scientific world has made in nuclear energy, and the problems involved in this field.

American Chemical Paint Opens West Coast Plant

The American Chemical Paint Company announces that it has acquired office and plant facilities on the West Coast, located at Niles, California, and expects to be operating there in November. Present plans include the production of metal-working chemicals (rust proofing and paint-bonding phosphate coating chemicals, pickling acid inhibitors) and agricultural chemicals.

Change of Address

The Organic Chemicals Division of Monsanto Chemical Company has moved from 1700 South Second Street to a new address at 800 North 12th Boulevard, St. Louis, Missouri.

* * *

The Auto City Plating Company has moved from 3450–3470 Denton Avenue to 197 South Waterman, Detroit, Michigan.

PERSONALS

Merritt L. Kastens has been appointed assistant to the Director of Stanford Research Institute, Stanford, Calif. Mr. Kastens had been associated with *Chemical and Engineering News* and *Industrial & Engineering Chemistry* since 1946 in San Francisco, Chicago and New York, and was Associate Editor when he resigned in July.

Martin H. Johnson is now in charge of Pioneering Research, Research and Development Division, Ray-O-Vac Company, Madison, Wis. He was formerly chief engineer of Continental Chemical Company, a Ray-O-Vac subsidiary, at Salem, Ore.

G. A. Nelson, manager of the Wyandotte Works of Pennsylvania Salt Manufacturing Company, has been assigned to general engineering and consultative work in connection with Pennsalt's current expansion and development plans. James M. McWhirter, formerly the company's Southern Works manager, succeeds Mr. Nelson.

C. P. Love, Kaiser Aluminum & Chemical Corporation, has recently been transferred to Tacoma, Wash., from the Chalmette Works, Chalmette, La.

Joseph Smatko is on leave of absence from the Department of Chemistry, University of Maryland, College Park, Md., and is currently Visiting Associate Professor and Acting Head of the Department of Chemical Engineering at the University of California, Los Angeles.

A. F. Garcia has been transferred from the Kaiser Aluminum & Chemical Corporation at Tacoma, Wash., to the company's plant at Chalmette, La.

Irwin Goldman has been appointed assistant to the manager of the Physics Laboratories at Sylvania Center, Bayside, N. Y. He succeeds Howard S. Moncton who has been made administrative engineer, Radio and Television Division, Sylvania Electric Products Inc.

V. C. Doerschuk, general manager of the smelting division of Aluminum Company of America since 1935, has been made technical consultant, chiefly

aluminum smelting and related problems. RAYMOND T. WHITZEL, formerly assistant general manager, succeeds Mr. Doerschuk.

DWIGHT E. COUCH has left the National Bureau of Standards in Washington, D. C., to accept a position as electrochemist with the U. S. Naval Ordnance Test Station at China Lake, Calif.

C. M. HOKE

Miss C. M. Hoke, Chemist and Advertising Manager of Jewelers Technical Advice Company, New York, and former vice-president and consulting chemist, Hoke, Inc., died on July 13. She made her home in Palisade, New Jersey.

Miss Hoke was born in Chicago, Illinois, in 1887 and received her A.B. degree from Hunter College in 1908 and A.M. in 1913 from Columbia University. Her chief interest was in industrial chemistry. She was one of the early women members of The Electrochemical Society, which she joined in 1927.

NEW MEMBERS

In September 1952 the following were elected to membership in The Electrochemical Society:

Active Members

HAROLD C. BEACHELL, Department of Chemistry, University of Delaware, Newark, Del. (Electric Insulation)

MARTHA J. BERGIN, Sylvania Electric Products, Inc., mailing add: 55 Fenwood Rd., Boston, Mass. (Electronics)

JOHN M. BLOCHER, JR., Battelle Memorial Institute, 505 King Ave., Columbus, Ohio (Electrothermics)

CLARK E. BRICKER, Department of Chemistry, Princeton University, Princeton, N. J. (Electrodeposition, Electro-Organic, and Theoretical Electrochemistry)

DAVID L. GAMBLE, New Jersey Zinc Company (of Pennsylvania), Technical Library, Palmerton, Pa. (Electrothermics)

KENNETH R. HESSE, Tel-O-Tube Corporation of America, 180 Van Riper Ave., East Paterson, N. J. (Electronics)

GEORGE IDRIS, Carnegie Institute of Technology, mailing add: Whitfield Hall, 5050 Forbes St., Pittsburgh, Pa.

RAMON I. LINDBERG, Sinclair Research Laboratories, Inc., Harvey, Ill. (Corrosion)

SIMON J. MORANA, The Beryllium Corporation, Box 1462, Reading, Pa. (Electronics)

FAUSTINO G. PRADO, Nickel Processing Corporation, mailing add: Nicaro, Oriente, Cuba (Battery and Electrodeposition)

JOSEPH M. SHERFEY, National Bureau of Standards, mailing add: 614 Nicholson St., N.W., Washington, D. C. (Electrodeposition)

DIMITRIOS N. STAICOPOULOS, E. I. duPont deNemours & Co., mailing add: 15 Valley Rd., Apt. 10, Drexel Hill, Pa. (Corrosion, Electronics, and Theoretical Electrochemistry)

C. H. TOENSING, General Electric Company, mailing add: 1331 Chardon Rd., Euclid, Ohio (Electronics and Electrothermics)

T. J. VARKEY, St. Joseph's College, Bangalore, S. India (Corrosion, Electrodeposition, and Industrial Electrolytic)

EMANUEL WOHL, Galvanic Products Corporation, mailing add: 3150 Rochambeau Ave., New York, N. Y. (Battery, Electrodeposition, and Electronics)

GWENDOLYN B. WOOD, National Bureau of Standards, Chemistry Bldg., Rm. 115, Washington, D. C.

Associate Members

NIRKEWAL S. BIRDIE, % D. C. M. Chemical Works, P.O. Box 1211, Delhi, India (Industrial Electrolytic)

JAMES F. CARRAHER, Cleveland Electric Illuminating Co., mailing add: 13301 Second Ave., East Cleveland, Ohio (Electric Insulation)

DOUGLAS PERRY, Louisiana State University, Box 6229, Baton Rouge, La. (Corrosion)

ALBERT R. SAWAYA, Willard Storage Battery Company, mailing add: 2602 Cedar Ave. #186, Cleveland, Ohio (Battery)

GEORGE SCHLOTZER, General Electric Company, mailing add: 15510 Huntmere Ave., Cleveland, Ohio (Electronics)

KURT H. STERN, Department of Chemistry, Clark University, Worcester, Mass. (Theoretical Electrochemistry)

NEIL D. VEIGEL, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio

Technical Research Engineer

Experienced man with mechanical and chemical engineering background. Should have strong bent for converting research results into workable industrial equipment; should also be able to carry out essential research in this connection. Versatility and energy are prime requisites. Initial effort will be in the field of high vacuum continuous coating.

Please send resume to:

NATIONAL RESEARCH CORPORATION

70 Memorial Drive **Cambridge 42, Massachusetts**

LETTER TO THE EDITOR

Electro-osmosis

Dear Sir:

Kogoro Murakoshi in his letter published in the September 1952 issue of the JOURNAL has apparently rediscovered "Electro-osmosis," first described by Reuss in 1808. He will find this invention included under the above name in textbooks discussing electrokinetics. References are numerous and include, for example: Glasstone, "Introduction to Electrochemistry," pp. 521–536; Dole, "Experimental and Theoretical Electrochemistry," pp. 454–457; MacInnes, "The Principles of Electrochemistry," pp. 424–426.

H. H. UHLIG

Massachusetts Institute of Technology, Cambridge, Massachusetts

BOOK REVIEW

ACIDS AND BASES—THEIR QUANTITATIVE BEHAVIOUR by R. P. Bell. Published by Methuen & Co. Ltd., London, 1952. vi plus 90 pages, $1.50.

This little book attempts a difficult task, a brief and unified account of some of the applications of the subject of acids and bases to chemical problems. The heart of the work is contained in two chapters devoted to the relation between molecular structure and acid

strength and the nature of acid base catalysis. Somewhat more than half of the work is a rather wordy review of material covered in many other places. The result is an overly brief and rather less unified treatment than the subject deserves. Extension of the work to twice the present size with a more complete indication of the various factors which operate in such systems would have increased the value of the book many fold.

As it stands it is difficult to see for whom the book has been intended. The brevity in the important sections prevents recommendation as a reference work, and as a course text it suffers from the fact that the level of treatment is not consistently maintained, the second half of the work assuming considerably more chemical and physical background than the first.

J. F. DEWALD

RECENT PATENTS

Selected for electrochemists by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

July 29, 1952

Gibbs, T. B., Dinerstein, S., and Gilman, G. W., 2,605,218, Electrolytic Method and Apparatus for the Manufacture of Tapered Conductors

Jacobson, H., 2,605,219, Preparation of Radioactive Bromine

Fonda, G. R., 2,605,227, Cadmium Phosphate Phosphors

Bodey, C. E., 2,605,296, Thermoelectric Generator and Casing Therefor

Dean, R. S., 2,605,297, Electrode for Electrical Systems

Marsal, P. A., 2,605,298, Dry Cell

Teas, J. P., 2,605,299, Primary Galvanic Cell

Shirland, F. A., Jr., 2,605,300, Graphite Molding Composition

August 5, 1952

Chester, A. E., 2,606,147, Electrodeposition of Arsenic

Portanova, M. J., and Rosinger, A., 2,606,148, Process for Electrolytic Preparation of Vanadium Oxide

Lamb, A. H., 2,606,215, Encased and Hermetically Sealed Photocell

August 12, 1952

Neish, R. A., 2,606,866, Method of Treating Tin Plate

Pianfetti, J. A., and Timmerman, R. W., 2,606,867, Gaseous Phase Photohalogenation of Hydrocarbons

Alquist, F. N., and Kauer, K. C., 2,606,868, Photochemical Preparation of the Delta Isomer of Benzene Hexachloride

Perret-Bit, R. J., 2,606,869, Electrolytic Cell

Ruben, S., 2,606,941, Primary Cell and Battery

Bonin, P. G., 2,606,942, Dry Battery

Roy, J. A., and Ives, R. S., 2,607,014, Electric Gaseous Discharge Device

LITERATURE FROM INDUSTRY

LUBRICATION PROCESS FOR COLD EXTRUSION. Described and illustrated in an 8-page booklet is a new phosphate coating and lubricating process which makes possible the cold extrusion and forming of both carbon and stainless steels. Detrex Corp. P-72

MOTOR SPEED CONTROLS. New bulletin describes in detail all of the Variac* motor speed controls. Technical information including speed-torque curves and typical applications is given on all models. General Radio Co.

* Registered trademark. P-73

BATTERY POWER REGULATOR. A new battery power regulator assures sustained accuracy and minimum battery maintenance when making measurements with company's Model DU Spectrophotometers. Permits precise control in regulating the charging unit so that the battery can be supplied with the exact amount of current needed for operating the instrument. Bulletin giving complete details, on request. Beckman Instruments, Inc. P-74

LABORATORY WASTE RECEPTACLES. In this foot-operated waste receptacle for laboratory use, the door is opened quickly and easily by foot pedal action (even when both hands are fully occupied) for immediate disposal of soiled filter paper, discarded glass slides, material samples, etc. When released, the door closes practically air-tight, eliminating offensive odors. Write for further information. United Metal Box Co., Inc. P-75

CHEMICAL PROPORTIONING PUMPS. Fully described in bulletin is a new chemical proportioning pump having these outstanding features: displacement of all liquid in the cylinder at every stroke, with stroke adjustable while the pump is running. Other important features listed. American I... strument Co., Inc. P-7...

METROGRAM BALANCE. Metrogram... a new high-capacity precision weighi... instrument, is described in illustrate... booklet. For testing, counting, com... pounding, laboratory and industri... weighing. Arthur S. La Pine & Co. P-7...

X-RAY SPECTROMETRY. New 4-pag... folder titled "X-Ray Techniques Ca... Help You Solve Your Materials Pro... lems" contains a technical article th... describes x-ray spectrometry with aut... matic chart recording as an importan... tool for solving today's materials pro... lems. Illustrated with drawings, chart... and photos. North American Philip... Company, Inc. P-7...

PEROXYGEN COMPOUNDS FOR TREA... ING METAL SURFACES. The variou... possibilities for use are outlined in ... new bulletin. Included are: treatment... to improve the adherence of finishes t... metal surfaces, to improve the ap... pearance of finished articles, and t... facilitate certain plating operation... Four general types of procedures a... covered. Becco Sales Corp. P-7...

LABORATORY SUPPLIES. Glass volu... metric apparatus and other scientif... equipment are described in the public... tion "Announcer," free on reques... Eberbach & Son Co. P-8...

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

EMPLOYMENT SITUATION

Please address replies to box shown... % The Electrochemical Society, Inc.... 235 W. 102nd St., New York 25, N. Y...

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ELECTROCHEMIST, Ph.D., industria... experience in deposition, corrosion... analytical instrumentation. Present sal... ary $6500. Desires position in industry... Available in 15-30 days. *Reply to Box... 350.*

Editorial

What Do We Mean by "Theoretical"

ONE often hears the expression, "That's all right in theory, but it doesn't work out in practice," or one of its many equivalents. In some environments, to call a man "theoretical" is a term of abuse. It, therefore, seems worthwhile, at the beginning of an issue of this JOURNAL which is under the auspices of the Division of Theoretical Electrochemistry, to discuss just what we mean by the term and, in particular, why it should have unpleasant overtones.

Actually, the most practical man uses theories. He may take a bus rather than go into the subway on the *theory*, i. e., a nonprovable supposition, that the bus will get him home quicker. Theories are our guides in a complicated world, so that our actions are not complete anarchy. In scientific research they help to direct our thought and our selection of experiments. They are "good" or "bad" depending upon whether they help or hinder our efforts to utilize nature for our own purposes. Applied, not-yet-applied, and nonapplicable scientific conclusions are all based on theories. The real opposition is not between "theoretical" and "applied" research, but between, as Dr. Conant puts it, "programmatic" and "uncommitted" investigations. Programmatic research is directed toward foreseeable, and usually immediately usable, ends. The investigator carrying out uncommitted research follows where his interest (and his theories) lead. It is a truism to say that many of the great industries that have transformed our world were based originally on researches of the latter type.

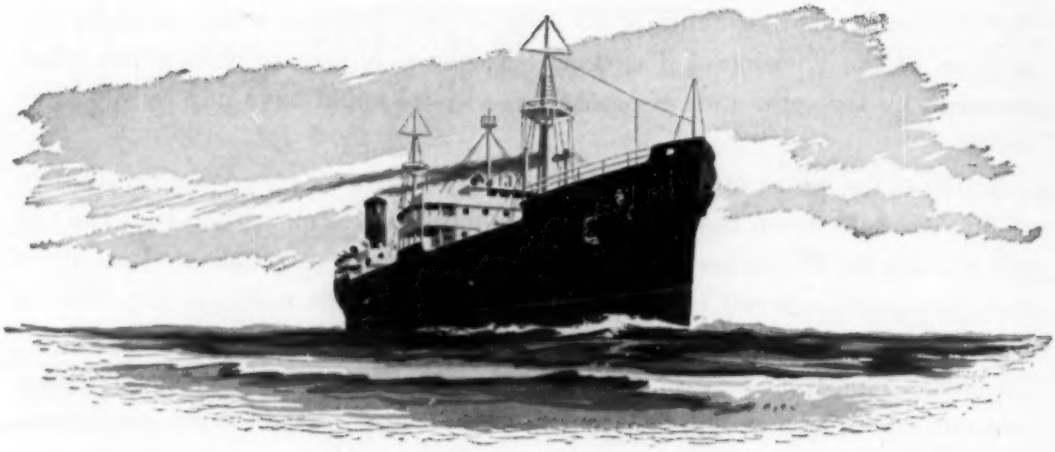
What then is the basis for the common derogatory use of the term "theoretical"? In some cases theories may not be helpful. Mostly the antagonism seems to be due to a more or less conscious recognition of the lag between the time of obtaining new scientific results and their being integrated into thought and practice. Attempts to catch up with, or even to understand, the newer results can be laborious and painful. The adapting of new ideas and processes to the current procedures is usually costly and time-consuming. It is much less taxing to the gray matter to dismiss the new developments with the epithet "theoretical" and to let someone else do the thinking and make the applications of the new results.

However, the utility and importance of uncommitted or basic research has become, in recent years, more and more evident to everybody, with the result that such research is, at long last, getting encouraging support and endowment. The lag between discovery and application is shortening until in some fields it hardly exists.

The question remains as to whether "theoretical" is the best term to describe the interests of this division. Maybe "exploratory" or "pioneering" would be better. However, the old term will probably stick, for a while at least.

—D. A. MACINNES

Electrochemistry at DOW



ELECTROCHEMISTRY goes to sea . . . to fight costly hull corrosion

Costly hull corrosion is now being controlled by an electrochemical method . . . cathodic protection.

This method has proved successful in combating corrosion in underground pipe lines, tanks and industrial equipment. Now it is being used, for the first time on a large American commercial vessel, by Dow on the "Marine Chemist," the 13,000 ton leased tanker which transports chemicals from Dow's Freeport, Texas plant to the east coast.

Hull corrosion results from small electric currents flowing through the sea from the more active to the less active parts of the hull, removing particles of metal from the active areas. This is prevented by transferring the current flow, and that's where cathodic protection comes in.

Magnesium anodes are installed on the sides of the ship's hull. Magnesium, a very active metal, becomes the most active area of the ship's hull, and current flows from it instead of the steel hull. Only the anodes, which can be inexpensively replaced, are corroded.

Dow's work in the development of cathodic protection is but one outstanding contribution of Dow, a producer of over 600 chemicals for industry and agriculture, in the field of electrochemistry.

THE DOW CHEMICAL COMPANY • MIDLAND, MICHIGAN

The magnesium anodes, shown here being installed on the "Marine Chemist," are about 20 inches in length and weigh 60 lbs. They were designed to last a year.

DOW

CHEMICALS

INDISPENSABLE TO INDUSTRY AND AGRICULTURE

Fiftieth Anniversary

FIFTY YEARS OF ELECTROCHEMICAL THEORY

Walter J. Hamer[1]

In many ways theoretical electrochemistry began with the work of Michael Faraday (1). His experiments on the conduction of an electric current through solutions demonstrated for the first time the existence of discrete particles of electricity, gave birth to the concept of atomic electricity, and started the development of theories of atomic structure. Today we believe that all matter is entirely electrical in nature and thus we may venture to say that all chemistry is in reality electrochemistry.

Faraday's laws are exact ones. His first law formed the basis of the international definition of the ampere during the last part of the nineteenth century and up to January 1, 1948 of the present one. The international ampere was defined as the quantity of electricity which flowing for one second would cause the deposition of 1.11800 milligrams of silver from a solution of a silver salt. Accurate values of the faraday in terms of the international definition were determined in 1914 by Vinal and Bates (2) using a standard form of silver coulometer, and by Washburn and Bates (3) in 1912 using an iodine coulometer. Studies of the deviations of electrode processes from Faraday's laws have served to elucidate mechanisms and to promulgate theories regarding processes that occur at electrode-electrolyte interfaces.

On January 1, 1948 the United States and other countries went over from international to absolute electrical units. When this conversion was effected, the ampere was defined in terms of the force produced by the current in a current balance (4) and no longer in terms of the weight of silver deposited in a coulometer in a given time. Nevertheless, the faraday constant remains one of the most important electrochemical constants.

In the past few years, new values of the faraday have been determined by two novel methods. Craig and Hoffman (5) devised what may be called an "oxalate coulometer" in which oxalate ion is anodically oxidized at gold electrodes to carbon dioxide. As a supply for oxalate ion, they used sodium oxalate of certified purity and which is used as an oxidation-reduction standard. Thus, Craig and Hoffman's determinations brought together chemical and electrical standards. Sommer and Hipple (6) have recently devised a method whereby the faraday is determined by a purely physical method. They used an instrument called the omegatron wherein the faraday is determined in terms of the gyromagnetic ratio of the proton and the cyclotron resonance frequency of an ion whose isotopic weight is known, both frequencies measured in the same magnetic field. Craig and Hoffman obtained a value of 96492 absolute coulombs per gram equivalent and Sommer and Hipple a value of 96497, both expressed on the chemical scale. Thus, we see that electrochemical and physical determinations of the faraday are in substantial agreement, with all the attendant significance that may be placed in the correlation of other universal constants (7), particularly Avogadro's number and the electronic charge. Thus, the cycle has been completed: electrochemical determinations have been tied in with chemical standards and with atomic phenomena. It is to be expected that many more correlations of fundamental constants will be forthcoming in the future as new methods are devised and older methods are perfected.

It is the consensus, however, that electrochemical theory had its beginning with the postulation of the electrolytic dissociation theory by Arrhenius (8) in 1887 and the work of van't Hoff and Ostwald who in the same year founded the Zeitschrift für physikalische Chemie. These three with their contemporaries are credited with the founding of modern electrochemistry and with the laying of the foundation of classical physical chemistry as a separate and primary division of chemistry. It is for this reason that theoretical electrochemistry is frequently considered to deal primarily with electrolytes. It is also for this reason that the major portion of this discourse will be devoted to electrolytes. Other phases of theoretical electrochemistry are the subject of other papers in this anniversary issue of the JOURNAL.

Early History of Electrolytes

Arrhenius postulated that the molecules of salts, acids, and bases which give solutions that conduct an electric current are partially dissociated into "free ions." He further postulated that these ions had no influence on each other and that their existence did not depend on an applied potential gradient. In the same year van't Hoff (9) made the monumental discovery that solutions which readily conduct an electric current possess colligative properties (freezing points, boiling points, osmotic pressures, vapor pressures) that are distinct from those solutions which do not readily conduct an electric current and therefore belong to a special class of systems. He also realized that a study of these systems was a branch of thermodynamics and made the first specialized application of thermodynamics to the subject. He showed that there exists an analogy between the osmotic pressure of a dilute solution and the gaseous pressure that the solute would exert if it existed in the form of a gas in the volume occupied by the solution.

Ostwald (10) a year later showed that some of these solutions obeyed a "dilution law," namely that the concentrations of the dissociated and undissociated molecules were in a ratio which was constant and independent of the stoichiometric concentration of the system. Following the proposal of Arrhenius, the degree of dissociation was considered to be given by the ratio of the equivalent conductance, Λ, of the solution at a particular concentration to the equivalent conductance at infinite dilution, Λ_o, where the electrolyte was considered to be completely ionized. Ostwald and van't Hoff's treatments, however, lacked generality and an exactness which could have been possible had they been familiar with the thermodynamics developed by Gibbs (11) in the United States ten years earlier.

Also, during this time, Nernst contributed to practically all phases of electrochemistry. He derived his well-known equation for electrode potentials as a function of concentration, assuming that a metal or gas possessed a tendency to pass from the atomic to ionic state which tendency he called the electrolytic solution pressure of the metal or gas (12). He also considered that the ions followed the analogy between

[1] National Bureau of Standards, Washington, D. C

osmotic pressure and gaseous pressure depicted by van't Hoff. Kohlrausch made extensive measurements of electrolytic conductivity, Hittorf continued his experiments on ionic mobility which he had started much earlier, Raoult (13) presented his famous law on vapor-pressure lowering, and Lorenz (14) contributed much to our knowledge of the state of ionic fluids. This group of workers was also adept at experimental techniques and the accuracy of their results was such that they were able to propose rules or laws now known to be substantially correct. Kohlrausch and Heydweiller (15) succeeded in making water of extremely high purity. Kohlrausch (16) predicted the square-root law of electrolytic conductivity shown many years later to be of the correct form by Onsager (17). He postulated the law of independent migration of ions. With Holborn and Dieselhorst, he (18) recommended values for the equivalent conductance of standard KCl solutions for the calibration of conductivity cells which compare favorably with those recommended 35 years later by Jones and Bradshaw (19).

Thus, at the turn of the century the theory of electrolytic dissociation was well entrenched. Both thermodynamic studies and electrical measurements tended to confirm the theory. Nevertheless, the theory was not universally accepted immediately without much argument. Kahlenberg (20) in addressing this Society at its first meeting in 1902, or 15 years after the advent of the theory stated that "the facts that flatly contradict the (Arrhenius) hypothesis are now so numerous that its doom is sealed." He based his views largely on the behavior of ampholytes, which were known to have colligative properties characteristic of electrolytes but conductivities which were typical of nonelectrolytes, and on soap solutions for which the reverse is true. Kahlenberg's views probably would have been different if Adams (21) and Bjerrum (22) had not waited until 1916 and 1923, respectively, to present their theories on "zwitterions" or hybrid ions and if the concept of "micelle" formation (23) had been known in 1902. Kahlenberg was also disturbed by the lack of correlation between the behavior of aqueous and nonaqueous systems, but in this, too, explanations came later in the Brønsted-Lowry theory of acids and bases (24, 25), which does much to correlate behavior in different solvents and in the Debye-Hückel (26) theory of interionic attraction, which shows the influence of dielectric constant on ionic behavior.

In 1908, Hering (27) inquired "what will happen if there are no electrodes to give ions their charge? Is the carrying of the charges by the ions the general and universal law, or is it only the law for the special case in which electrodes are used? Is it a primary action, or is it merely a consequential one due to the use of electrodes?" On the other hand, Bancroft (28) stated "since a theory can only be displaced by another theory, the electrolytic dissociation theory will hold the field until a better one is brought forward." One suspects, however, that the great debate that ensued on the electrolytic dissociation theory involved a certain amount of misunderstanding. It is not clear whether the opponents of the theory denied the existence of ions or whether they in reality opposed the second postulate of Arrhenius that oppositely charged ions had no influence on each other. In any case the problem has been resolved, although we still speak of Arrhenius' hypothesis as the "electrolytic dissociation theory" and not as the "electrolytic dissociation law."

Another argument that the proponents of the dissociation theory had to face was that there were certain anomalies in the degree of dissociation as determined by the Arrhenius' ratio, Λ/Λ_o, and certain deviations from Ostwald's dilution law that seemed difficult to explain (29). Their u-e led to t main conclusions. First, values of the degree of dissociati of electrolytes fell into two distinct groups, some high a some low instead of a wide dispersion in values. Second, so types of electrolytes followed Ostwald's law; others did n Attempts to reconcile these observations were largely empiri and unsatisfactory. It is true that many felt that "electr static forces" were responsible for the anomalies but a sat factory solution of such forces was not immediately for coming. Noyes (30) was the first to suggest that electroly must be classed into two groups: those completely dissociat into ions at all concentrations (strong electrolytes) and th incompletely dissociated (weak electrolytes). Bjerrum (3 Sutherland (32), and Lewis (33) shortly thereafter concurr in this classification which is now universally accepted. T x-ray studies of Bragg (34) and others on the structure crystals of the NaCl type, whereby it was proven that t crystals consist of ions in a lattice and that no molecules a present, was probably greatly responsible for the final a ceptance of the idea that certain salts, when dissolved water, were completely ionized at all concentrations and n merely at infinite dilution. Also, that electrostatic forc between charged ions are responsible for the stability of crystal has been established on the magnitude of the spa lattice energy by calculations of Born, Fajans, Madelun and Debye and Scherrer (35).

Accepting the view that electrolytes fell into two grou solved one problem, namely, why certain compounds did n obey the Ostwald dilution law which involves the concentr tions of dissociated and undissociated molecules. It did n solve, however, the question why the equivalent conductanc of *strong* electrolytes decreased with increases in the concen tration of the solution.

Views on these problems were many and varied. It w thought or suggested that the observed variations in condu tivity were due to changes in viscosity of the medium, t "ion hydration," to increased ionization of the solvent c addition of the salt, to complex-ion formation, to changes i the ionizing power of the medium, and to other factors (36 That viscosity had or should have an influence on electr lytic conductivity was believed for a long time (37, 38). I 1906, Walden (39) stated that the product of the limitin equivalent conductance of an electrolyte and the viscosity o the solvent should be a constant, and presented data in sub stantiation. He was led to this view on the basis that if a infinite dilution separate ions move independently, then thei motion should depend only on their nature and on the so vent. Kraus and Bray (40) showed that this relation was no followed accurately. Some felt that the relation was to b expected in light of Stokes' law, but would not be expecte to hold completely unless the ions existed as spheres.

The question of "ion hydration" was considered at grea length in the early years of this century. One famous scien tist tried to explain all deviations from ideality by a "hydra tion theory" but it was later shown that more water had t be adsorbed by the ions than was actually present in the solu tion. A popular method to determine "ion hydration" was t conduct experiments on ion transport using solutions con taining an inert nonelectrolyte which was considered not t migrate under a potential gradient. This idea was first sug gested by Nernst (41) and extensively studied by many (42) In this method, no absolute value of the extent of hydratio of an ionic species is attainable but by assuming the amoun of hydration for a reference, for example the hydrogen ion Washburn was able to construct a table giving the degree o

dration of various ions. However, Longsworth (43) conted experiments in 1947 that have thrown doubt on our ncepts of "ion hydration." He used a series of supposedly ert nonelectrolytes (raffinose, mannitol, resorcinol, and ea), added these to electrolytes and conducted transference periments by the technique of moving boundaries, and trapolated the data in each case to zero concentration of nelectrolyte. He did not, however, obtain convergence of e data. In other words, in the limit of zero nonelectrolyte ncentration he was unable to obtain unequivocal values of e degree of hydration of any ion. Therefore, either the nonctrolyte moves or is carried by the ion, or affects the elecstatic forces between the ions in some fashion not yet idated. In any case, it would appear that "ion hydran" is a misnomer. One wonders why so many insist that e proton exists in water as the hydronium ion, H_3O^+, when conclusive proof of this has been presented. To the follow- question from H. S. Taylor (44) in 1927, "To summarize en, the present status of the hydration problem, it is this: e hydrogen ion is probably hydrated; it is apparently buried a water molecule; the other ions are not hydrated (chemilly) at all, but are surrounded by oriented water molecules d carry these with them when they move. Is that a correct derstanding of the picture at the present time." Peter bye answered, "Yes." Today, Longsworth would probably so answer, "Yes."

Various equations were proposed for use in extrapolations infinite dilution to obtain Λ_o. Some used the square root the concentration, others the cube root, others the logathm, and still others some complex function of the concenation. Various dilution law equations were proposed, among hich we may list:

$$c\alpha^2/(1 - \alpha) = K$$

$$c\alpha^2/(1 - \alpha) - k(c\alpha)^n = K$$

$$c\alpha^2/(1 - \alpha) - k\{[(1 - \alpha)c]^{1/2}\}^p = K$$

$$\log \Lambda_c^2/\Lambda_o(\Lambda_o - \Lambda) - k(c\Lambda/\Lambda_o)^h = K$$

here n, k, p, and h were empirical constants, K the dissociaon constant (45, 46, 47, 48), and $\alpha = \Lambda/\Lambda_o$.

In addition to the above explanations for the variations conductance and the dissociation constant with electroe concentration other explanations were presented, includg the attempts to correct for the deviations of the ions from eir behavior based on the analogy with the gas laws. In any of these attempts, references to "electrostatic effects" to "electrical forces which come into play in a medium ntaining charged particles" (36) were seen, but a fundaental treatment of them was lacking until 1923 when Debye nd Hückel (26) presented their important paper on the eory of interionic attraction. Van Laar (49), Hertz (50), hosh (51), and Milner (52) previously had recognized the oblem of coulombic forces in solutions of electrolytes but ly Milner visualized the problem correctly. However, his eatment was involved, required graphical approximations, nd did not yield an entirely satisfactory solution. Debye nd Hückel's treatment, interestingly enough, included the scosity factor discussed above, the dielectric constant of e solvent, the concentration, and the temperature, and veral universal constants. It served to correlate the mass data available at the time of its presentation.

Concurrently, with these developments in the treatment electrostatic forces and with extensive studies of electroic conductivity, numerous attempts were made to develop a system of solution thermodynamics which would be exact and sufficiently simple to reduce numerical computations to a minimum. Of these, the one devised by G. N. Lewis (53) proved to be the most satisfactory and has been universally adopted. Certainly, the work of Lewis and his associates from 1912 to 1928 served to crystallize and integrate the theoretical and experimental parts of solution thermodynamics into an exact science. In this development it was shown conclusively that the phenomena responsible for the lowering of vapor pressure, depression of the freezing point, or variation of electromotive force with dilution are the same.

Also, in this work much use was made of galvanic cells to obtain heats and free energies of formation, reaction, transfer, or dilution. Among many, one series of studies on galvanic cells was of outstanding importance, and was one in which electrochemists may take pride. In 1903, T. W. Richards (54) from the study of many types of galvanic cells over a wide range of temperatures observed that ΔH, the heat of reaction, and ΔF, the change in free energy, approached each other in value as the temperature was lowered. Shortly thereafter, Nernst (55) announced his "heat theorem" which may be stated as—for any reaction in a condensed system values of $\delta(\Delta H)/\delta T$ and $\delta(\Delta F)/\delta T$ become zero in numerical value at the absolute zero, from which it follows that ΔC_p and ΔS are also zero at the absolute zero of temperature. In 1912 Planck (56) generalized the Nernst heat theorem by postulating that the entropy of a pure solid or pure liquid is zero at absolute zero. This statement forms the basis of what is known as the *third law of thermodynamics*. Thus we see that there is every reason to believe that it was electrochemical investigations that led to this important law.

During the past fifty years, therefore, we may say that the development of thermodynamics of electrolytes and the treatment of the electrostatic forces inherent in all electrolytes were of profound importance in that they stimulated scientific thought and influenced the direction of scientific research. Application of the principles inherent in both were applied to electrode reactions and electrolytic processes. Accordingly, we shall consider each further.

Thermodynamics and Electrolytes

Lewis' system of thermodynamics was implicit in the work of J. Willard Gibbs but Lewis succeeded in simplifying the procedures. He also introduced two new concepts for condensed systems, namely, the activity and activity coefficient which he related to the free energy of the components of a solution.

For closed systems in which no matter is added or withdrawn thermodynamics give:

$$dE = TdS - pdV \qquad \text{(I)}$$

where E is energy, T the absolute temperature, S the entropy, p the pressure, and V the volume. For an open system to which matter may be added or withdrawn (for example, addition of a salt to water or removal of water from a salt solution by evaporation) Gibbs gave:

$$dE = TdS - pdV + \mu_A dn_A + \mu_B dn_B + \cdots \mu_Z dn_Z \qquad \text{(II)}$$

where n represents the number of moles of component A, B, etc., represented by subscripts and the μ's represent the Gibbs' "chemical potentials" of the various components. Since from thermodynamical considerations, $F = E - TS + pV$, $H = E + pV$ and $A = E - TS$ (F = free energy, H = heat content, and A = work content), the Gibbs'

"chemical potentials" for component A, for example, may be defined in a multiplicity of ways as follows:

$$\mu_A = (dE/dn_A)_{S,V,n'} = (dH/dn_A)_{S,p,n'}$$

$$= (d\Delta/dn_A)_{T,V,n'} = (dF/dn_A)_{T,p,n'} \quad \text{(III)}$$

where n' represents the constancy of all components except component A. Thus, Gibbs' "chemical potential" could be expressed in various ways depending on what conditions are held constant during an experimental measurement. Lewis chose the last equality (or definition) in his definition of activity. This was a natural and logical choice because we can easily design experiments wherein the temperature and pressure are maintained constant. We all realize that it is inconvenient to conduct experiments at constant volume and temperature, under which conditions the third equality of equation (III) would apply; and it is indeed difficult to conceive of ways to conduct experiments either at constant entropy and pressure (second equality) or at constant entropy and volume (first equality).

Lewis proposed the symbol $\overline{F}_A$ for Gibbs' chemical potential defined as $(dF/dn_A)_{T,P,n'}$ where $\overline{F}_A$ is the partial molal free energy of component A in a system composed of n components. Similar partial molal free energies may be represented for other components of the solution. As absolute free energies or partial free energies cannot be obtained, Lewis defined activity by the equation:

$$\overline{F}_A - \overline{F}^o_A = RT \ln a_A \quad \text{(IV)}$$

where $\overline{F}^o_A$ is the partial molal free energy of a component A in some arbitrary standard state. The standard state is chosen so that the ratio between the activity and the concentration is equal to unity at infinite dilution where the laws of ideal solutions are obeyed. Lewis called this ratio the activity coefficient, f_A, thus $a_A = N_A f_A$ and it gives a measure of the deviations of solutions from ideality and would include the magnitude of all effects that lead to these deviations. Concentration units other than mole fraction n could also be used in this definition. In that case, the activity coefficients would have different values (57).

As electroneutrality must prevail in electrolytic solutions, the activity of a salt that ionized into ν_+ cations and ν_- anions is given by:

$$a_{salt} = a_+^{\nu_+} \times a_-^{\nu_-} = a_\pm^{\nu}. \quad \text{(V)}$$

Therefore, for a salt solution, its mean activity, $a_\pm$, would be given by:

$$\overline{F}_A - \overline{F}^o_A = \nu RT \ln a_\pm \quad \text{(VI)}$$

where $\nu = \nu_+ + \nu_-$.

We would also have an expression similar to equation (IV) for the solvent in the salt solution. If we let the subscript 1 denote solvent and the subscript 2 denote solute, the relation between the activity of the solvent and the solute is given by the Gibbs-Duhem equation which may be expressed in the form:

$$N_1 \left(\frac{\partial \ln a_1}{\partial N_1} \right)_{P,T} = -N_2 \left(\frac{\partial \ln a_2}{\partial N_1} \right)_{P,T} \quad \text{(VII)}$$

where N represents mole fraction. Thus, we can calculate the activity and thence the activity coefficient of a solute from either its own escaping tendency or from that of the solvent in which it is dissolved.

During the past 25 years a number of experimental methods have been developed or perfected for the accurate determination of activity coefficients. These are based on: (*a*) freezing-point depression, (*b*) boiling-point elevation, (*c*) vapor-pressure lowering, (*d*) isopiestic or vapor-pressure equilibration, (*e*) emf of galvanic cells without liquid junction, (*f*) transference numbers and emf of galvanic cells with liquid junction, and (*g*) solubility. The first four involve measurement of the escaping tendency of the solvent and the subsequent evaluation of the solute activity through the Gibbs-Duhem equation. The last three give a direct measure of the solute activity. The solubility method (58) is generally applicable only to sparingly soluble salts and therefore is infrequently used.

The freezing-point method has been perfected by Scatchard and associates (59) and the boiling-point method by R. P. Smith (60). The latter method is more difficult experimentally and the molal boiling-point elevation is less than the corresponding freezing-point depression. Even so, Smith employed the method with remarkable success. By varying the external pressure he was able to vary the boiling point and thereby obtain data over a considerable temperature range from that of the normal boiling point. The freezing-point method has the disadvantage that it can yield data only at the freezing point. However, data at other temperatures may be calculated providing the relative partial molal heat contents of the solutions are known. In recent years, Robinson (61) and Gucker (62) and their associates have contributed such data to the literature.

The vapor pressure method is experimentally difficult to use when high accuracy is desired. For static measurements all permanent gases must be removed from the vapor phase. Even so, Shankman and Gordon (63) used the method with success to determine the activity coefficients of sulfuric acid. The method is not an independent one. Since measurements cannot be made with sufficient accuracy for dilute solutions to permit extrapolation to the standard state (infinite dilution) an activity coefficient determined by some other method must be chosen for a particular concentration (preferably dilute) and used in lieu of extrapolation. Thus, Shankman and Gordon employed the value for the activity coefficient of 0.1 molal H_2SO_4 obtained from measurements of galvanic cells without liquid junction by Harned and Hamer (64). The dynamic vapor-pressure method has not yet been developed to a high state of precision although Bechtold and Newton (65) developed an automatically controlled dynamic method that gave qualitative results.

The isopiestic method was developed by Robinson and his associates (66). In this method the vapor pressure of the solvent over a solution of unknown activity is compared or matched against that of a solution of known activity, whereby isopiestic or isotonic solutions are obtained having the same activity. Obviously, this is a relative method, as the activity of the reference solution must be determined by another method. It is, however, a convenient method and ideally suited to concentrated solutions. In fact, Scatchard, Hamer and Wood (67) used the method to determine accurate values of the solubility of highly soluble salts, such as KCl and NaCl. A method involving measurements of vapor pressure through isothermal equilibration in the vapor phase, proposed by Stokes (68), has not been tested sufficiently to warrant classifying it as a precision method.

Galvanic cells without liquid junction have probably been used more than the other methods for the determination of activity coefficients, because they are relatively easy to assemble, may be used at low and high concentrations, may be applied over a wide range of temperatures, and give

direct measure of the activity coefficient of the solute. It is true that for dilute solutions gases must be excluded and corrections for electrode solubility must be made if accurate values of activity coefficients are desired. This method has been used by many, especially Harned and his students (69).

The method for obtaining activity coefficients from cells with liquid junction was devised by MacInnes and his associates (70). In this method cells of the type:

$$\text{Ag, AgCl} \mid \text{NaCl } (c_1) \mid \text{NaCl } (c_2) \mid \text{AgCl, Ag}$$

are used. A liquid junction exists between the two solutions of NaCl of different concentration. For cells of this type the emf is given by

$$E = -\frac{2RT}{\mathbf{F}} \int_1^2 T_+ \, d \ln a_\pm \qquad \text{(VIII)}$$

where the integration extends from concentrations [I] to [II]. To obtain values of $a_\pm$ by this method, accurate values of T_+, the transference number, are needed, and such are available from the work of Longsworth and MacInnes (71). This method is especially well adapted to dilute solutions.

These methods have been extensively used to obtain the activity coefficients of strong electrolytes over a wide range of temperature and concentration. That these quantities are valuable is attested to by the fact that Kortüm and Bockris (72) in their book on "Electrochemistry" have devoted 27 pages to tables giving numerical values of activity coefficients; Harned and Owen (69) in their book on "The Physical Chemistry of Electrolytic Solutions" devoted 32 pages to this purpose.

Whereas the thermodynamics of strong electrolytes is determined by various methods, electrochemical methods are primarily used in studying the characteristics of weak electrolytes. This is because weak electrolytes are only partially dissociated into ions and accurate methods must be used to determine the extent of this dissociation. Electrochemical methods serve this purpose. In 1932 two electrochemical methods were devised for accurate determinations of ionization constants: the conductivity method of MacInnes and his associates (73), and the electromotive-force method of Harned and his students (74). These two methods were initially applied to the determination of the ionization constant of acetic acid at 25°C. Agreement as to value was remarkable. Harned and Ehlers obtained 1.754×10^{-5}; MacInnes and Shedlovsky 1.758×10^{-5}.

In his method, MacInnes used as a degree of dissociation Λ/Λ_e instead of Λ/Λ_o as done by Arrhenius, where Λ is the equivalent conductance at concentration c and Λ_e is the equivalent conductance of the electrolyte in a completely dissociated condition and at the ion concentration $c\alpha$. Λ_e is obtained using the Kohlrausch principle of independent ion migration and the assumption that solutions of alkali salts and inorganic hydrogen acids are completely dissociated into ions, both of which have been substantiated by experimental data. For acetic acid, for example, the procedure would be as follows: (*a*) measure the equivalent conductance of acetic acid (HAc) at a series of concentrations; (*b*) measure the equivalent conductances of sodium acetate (NaAc), HCl, and NaCl also at a series of concentrations; (*c*) calculate Λ_{eHAc} from the relationship

$$\begin{aligned}\Lambda_{eHAc} &= \lambda_H + \lambda_{Ac} \\ &= \lambda_H + \lambda_{Cl} + \lambda_{Na} + \lambda_{Ac} - \lambda_{Na} - \lambda_{Cl} \qquad \text{(IX)}\end{aligned}$$

which follows from the Kohlrausch principle and in which λ represents the ionic conductances of the ions denoted by subscripts; (*d*) calculate values of $\Lambda_{HAc}/\Lambda_{eHAc}$ which would give values of the degree of dissociation of the acid; and (*e*) use these values in the mass action law to obtain values of the dissociation constant of acetic acid. In this procedure the ratio $\Lambda_{HAc}/\Lambda_{eHAc}$ must be determined at the ionic concentration and not the stoichiometric concentration. This entails a short series of approximations since the ionic concentration cannot be known a priori. The method has yielded good results. It has not yet been applied to dibasic or polybasic acids where complications would arise owing to the complexity of the ions that may be present in the solutions, especially if the ratio of the ionization constants is small.

The emf method of Harned and students is well adapted to measurements at various temperatures and entails measurements of the emf of cells of the type:

$$\text{Pt, } H_2(g) \mid \text{HAc}(m_1), \text{ NaAc}(m_2), \text{ NaCl}(m_3) \mid \text{AgCl}(s), \text{ Ag}(s)$$

which is a cell without liquid junction or rather one with negligible liquid junction as shown by Beattie (75). Here the electrodes are reversible to HCl even though other ions are present, and the emf, therefore, gives a measure of the free energy of formation of HCl (or dilution, in comparisons) in the presence of the other ionic constituents. This fact is frequently overlooked in the literature.

The expression for the emf of this cell as a function of the concentrations of hydrogen and chloride ions is then combined with the expression for the ionization constant of the acid to give:

$$\frac{(E - E^\circ)\mathbf{F}}{2.3026\,RT} + \log \frac{m_3(m_1 - m_H)}{m_2 + m_H} + 2A\sqrt{\mu} = -\log K + B\mu \qquad \text{(X)}$$

wherein the limiting law of Debye and Hückel plus an empirical term linear in the ionic strength, μ, is used to represent the ionic activity coefficients involved. On extrapolation to infinite dilution, where $B\mu = 0$, of the values of the left side of equation (X) obtained for a series of concentrations, values of $-\log K$ or pK and hence K are obtained.

Harned and associates have applied this method to the determination of the dissociation constants of a large number of acids, bases, and ampholytes in various water-nonaqueous solvents and over a wide range of temperature, usually 0° to 60°C. In this determination, values of m_H have to be obtained by a short series of approximations. First, extrapolations are made to infinite dilution by assuming that m_H is zero; then the provisional K value thus obtained is used in the expression for the dissociation constant and a provisional value of m_H is obtained which is used in equation (X), and the operations repeated until self-consistent values of m_H and K are obtained. This procedure is not necessary in determining the dissociation constant of water for which m_H is of the order of 10^{-7} and therefore a negligible correction (76). The procedure is satisfactory only if K is less than 1×10^{-5}. For other cases, divergence of values at infinite dilution does not result, if the extended equation of Debye and Hückel is used to express the ionic activity coefficients involved, and various values of the "closest distance approach," a_i, of the ions are employed. This is illustrated for formic acid in Fig. 1. Here values of 0, 4, 8, 20, and ∞ have been used for the "closest distance approach" of the ions. It is evident that convergence is not obtained (77) at zero ionic strength. When a_i is 0, K is 1.785×10^{-4}; when a_i is 4, K is 1.781×10^{-4}; when $a_i = 20$, K is 1.773×10^{-4}, etc. (77). For acids of lower dissociation constants, the errors from this

source are negligible; for acids of higher constants, the errors are correspondingly greater. For example, the first ionization constant of phosphoric acid (78), using a 1–1 buffer ratio, is 7.435×10^{-3} when a_i is 0 and 7.163×10^{-3} when a_i is 4. The reason for the lack of convergence lies in the fact that extrapolations must be made through points representing various buffer ratios as the m_H corrections alter the stoichiometric concentrations. The method is a convenient and accurate one for determinations of dissociation constants of

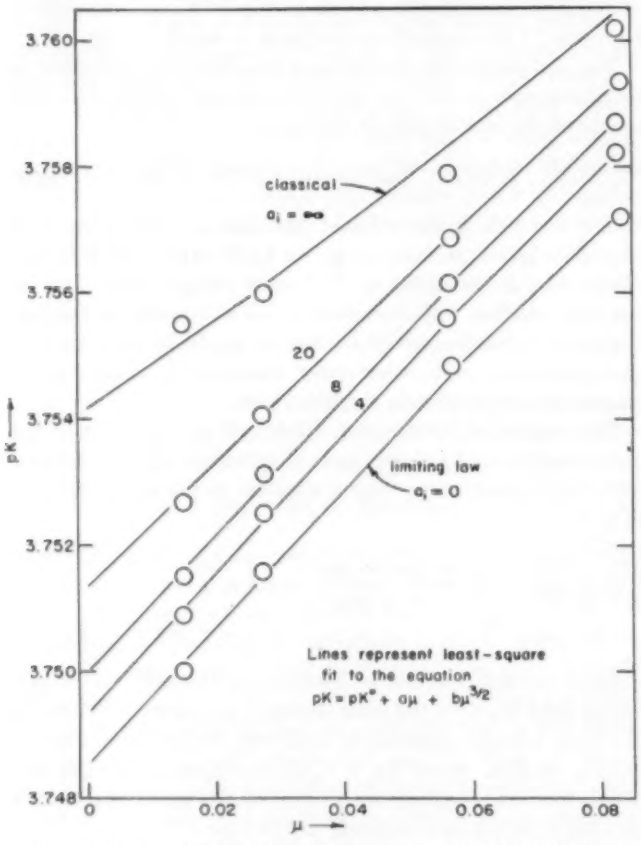


FIG. 1. Data showing lack of convergence in the limit of zero ionic strength for determination of dissociation constant for formic acid. Left side of equation (X), pK′, plotted against ionic strength; $2A\sqrt{\mu}/(1 + \beta a_i\sqrt{\mu})$ used instead of the term $2A\sqrt{\mu}$.

smaller magnitude than 10^{-5} and gives fairly quantitative values for the others since one may assume that 4 Angstrom units would be a fair guess to use for the "closest distance of approach of the ions." The data on formic acid are included here to show that the Debye-Hückel theory cannot be used indiscriminately; it is not a panacea for dilute solutions. In the present case, the law may be applied if some method was known for the determination of the hydrogen-ion concentrations of the solutions.

Harned and Embree (79) gave the equation

$$\log K - \log K_m = 0.00005(T - T_m)^2$$

for the variation of ionization constants with temperature, wherein K_m and T_m are empirical constants. K_m represents the maximum value obtained for K, and T_m the temperature at which this occurs. It is interesting that this equation predicts that the dissociation constant of all weak electrolytes would pass through a maximum at some temperature.

Another quantity that aids in interpreting weak electrolytes was proposed during the period which we are concerned and that is the *p*H symbol proposed by Sørensen (80) in 1909. Sørensen originally defined *p*H as

$$pH = -\log c_H. \qquad (XI)$$

There probably could be no contention with this definition in colorimetric determinations of *p*H if absolute standards could be used instead of reference standards calibrated on the basis of measurements of galvanic cells. Most *p*H measurements are based today on electrochemical methods involving the use of some form of galvanic cell. It is now well realized that the potential at a hydrogen electrode, or at electrodes that function as hydrogen electrodes, is related not to hydrogen-ion concentration but to hydrogen-ion activity. It is further realized that equilibrium and kinetic expressions involve, for the most part, ion activities. Therefore, it is essential that the *p*H scale be placed as closely as is experimentally feasible to the thermodynamic requirements. Unfortunately, values of single-ion activities or activity coefficients are as thermodynamically inassessable as are single electrode potentials or the potentials at double layers.

Nevertheless, it has been realized that attempts should be made to define *p*H in terms which will at least approximate the results that would be obtained by methods known to be thermodynamically sound. With this psychology, Hitchcock and Taylor (81) and MacInnes, Belcher, and Shedlovsky (82) devised a method wherein the *p*H scale is standardized in terms of known values of the thermodynamic dissociation constants of weak acids. In essence the method is this: a buffer solution, say of acetic acid and sodium acetate, is made up in a number of dilute solutions. These are placed successively in a galvanic cell composed of a hydrogen electrode and a normal or saturated calomel half-cell, wherein the buffer solution forms a liquid junction with the KCl of the half-cell. Upon extrapolation to zero concentration (Hitchcock and Taylor, and MacInnes, Belcher, and Shedlovsky's methods differed somewhat) of suitable functions involving the measured emf and assuming no variation in liquid junction potentials with concentration, they obtained a value for the potential of the calomel half-cell. Since the dissociation constant of the acid is well known (see above), the value of the calomel half-cell when used in the reverse procedure described above would yield the same dissociation constant as the method without liquid junction and by which thermodynamic dissociation constants are obtained. In other words, if the cell of MacInnes, Belcher, and Shedlovsky with liquid junction and the method of Harned and associates involving cells without liquid junction were used to measure the dissociation constant of a new acid, the same result would be obtained by the two methods. This method is adaptable only to weak buffer solutions; strong acids for which negative *p*H values may be obtained require a different potential value for the calomel half-cell (83) largely because of differences in the liquid-junction potentials involved.

Another method (84) for standardization of the *p*H scale involves measurements of cells of the type:

$$Pt,\ H_2(g)\ |\ \text{solution} + NaCl\ |\ AgCl(s),\ Ag(s)$$

following suggestions originally made by Guggenheim (85) and by Hitchcock (86). By rearrangement of the Nernst equation for the emf of this cell we have:

$$pH = \frac{(E - E^\circ)\mathbf{F}}{2.3026\ RT} + \log m_{Cl} + \log f_{Cl} \qquad (XII)$$

on the assumption that $f_H f_{Cl}$ may be separated. This method gets around the troublesome liquid-junction potential but

volves the estimation of the activity coefficient of the Cl^- ion. By making reasonable assumptions, however, and using dilute solutions, *p*H values of reasonable reliability may be obtained by this method (87). Another method (88) based essentially on the law of variation of activity coefficients at constant total molality (89) may be employed to convert values of $(-\log m_H f_H f_{Cl})$ directly obtainable from above cell to $(-\log m_H f_H)$ or *p*H. From measurements of $(-\log m_H f_H f_{Cl})$ on KOH solutions (basic side of scale) and HCl (acid side of scale) by the above cell and for which $(-\log m_H f_H)$ is known it is possible then to compare $(-\log m_H f_H f_{Cl})$ and $(-\log m_H f_H)$ for an unknown solution. In this method, it is assumed that $f_H = f_{Cl} = f_{HCl}$ an assumption originally proposed by Guggenheim (90).

These methods have been applied to the determination of the *p*H at 25°C of 0.05 molal potassium acid phthalate, used extensively in the calibration of *p*H meters, with the following results:

Method with liquid junction

H and T (81)	= 4.008
M, B, and S (82)	= 4.000

Method without liquid junction

Method No. 1 (84)	= 4.005
Method No. 2 (91)	= 4.008.

We can, therefore, say that the *p*H of 0.05*M* potassium acid phthalate is 4.01 at 25°C, or 0.04 pH unit higher (neglecting the small difference in temperature; Clark and Lubs' value was for 18°C) than the value given by Clark and Lubs (92) on the old basis of apparent hydrogen-ion concentration. This value is now widely used in this country and abroad (93). The method involving measurements of cells without liquid junction is well suited to measurements of relative *p*H values over a wide range in temperatures. By its use it has been found that high *p*H values decrease and low *p*H values increase (94) with increases in temperature in a fashion to suggest that all solutions would have an identical *p*H at the critical temperature of water and of a value approximating that of the solvent alone (95).

Interionic Attraction

Simultaneously with the development of exact methods to treat the thermodynamics of solutions, the past fifty years have seen the evolution of an electrostatic and hydrodynamical theory of electrolytes developed largely through the application of statistical mechanical methods. In this development, the Boltzmann distribution law has played a dominant role. Debye and Hückel used the law in their theory of interionic attraction and Eyring and others in the development of the theory of absolute reaction rates.

The theory of Debye and Hückel (26) concerning interionic attraction is probably the most noteworthy contribution to theoretical electrochemistry of the past fifty years. It has had a profound effect on scientific thought and influenced the course of electrochemical investigations in an infinite number of ways. The essential postulate of their theory was the concept of the "ion atmosphere." In essence Debye and Hückel considered that on a time average any ion would be surrounded by a greater number of ions of opposite charge than like charge, as a result of the attraction between electrical charges of unlike sign and the repulsion of charges of like sign, both of which follow Coulomb's law of charged bodies. At a distance from an ion, therefore, would be an "ionic cloud" of opposite charge which will set up a field of potential whose magnitude will depend on the distance of the "cloud" from the central ion.

Thermal vibration of the ions will tend to disturb this arrangement but not entirely so, and Debye and Hückel used the Boltzmann principle to express the ionic distribution as a function of the ratio of the electrical and thermal energies. Debye and Hückel also had the foresight to see that Poisson's equation could be used to express the relation between the potential and the average electrical density. On these principles and with some simplification in mathematics, they arrived at the equation:

$$\frac{1}{\kappa} = \left(\frac{1000\, k\epsilon T}{4\pi e^2 N \Sigma c_i z_i^2}\right)^{1/2} \qquad \text{(XIII)}$$

for the thickness $1/\kappa$ of the ion atmosphere, where ϵ is the solvent dielectric constant, T the absolute temperature, k the Boltzmann constant or gas constant for a single molecule, N the Avogadro number, e the electronic charge, z the ionic valence, and c the concentration in moles per liter. It is interesting to note that $\Sigma c_i z_i^2$ is the ionic strength, μ, introduced two years earlier by Lewis and Randall (96) to aid in correlating the properties of electrolytic solutions. For a 0.1 molal solution at room temperature the thickness of the ion atmosphere is the order of 1 Angstrom unit or 10^{-8} cm.

By several mathematical steps which need not concern us here, by assuming that all deviations from the behavior of ideal solutions could be attributed to electrical charges on the ions, and by calculating the free energy changes associated with the charging and discharging of an ion and its transfer from a dilute to a more concentrated solution, Debye and Hückel [see also Güntelberg (26a)] derived the following equation for the activity coefficient of an ion as a function of its concentration:

$$-\ln f_i = \frac{Z_i^2 e^3 \sqrt{\pi N/1000\, \Sigma c_i z_i^2}}{(\epsilon kT)^{3/2}(1 + a_i \sqrt{4\pi N e^2 \Sigma c_i z_i^2/1000 \epsilon kT})} \qquad \text{(XIV)}$$

other symbols have the same significance as given above for the ionic atmosphere. This equation may be put in the form:

$$-\log f_i = \frac{A\sqrt{\mu}}{1 + \beta\, a_i \sqrt{\mu}} \qquad \text{(XV)}$$

which reduces to the limiting form

$$-\log f_i = A\sqrt{\mu} \qquad \text{(XVI)}$$

for very dilute solutions, equivalent to a zero value for a_i.

Later, Hückel (97) modified this equation (XV) by adding an empirical term linear in the ionic strength to give

$$-\log f_i = \frac{A\sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} - B\mu. \qquad \text{(XVII)}$$

Hückel considered that the theory requires the dielectric constant of the solution rather than that of the solvent. He believed that the dielectric constant decreased linearly with solute concentration. The value of B must be determined from experiments; no method is yet known whereby it can be calculated from physical data.

Analysis of the assumptions and approximations made in the Debye-Hückel theory have been made by Kramers (98), Fowler (99), Kirkwood (100), and Gronwall, LaMer, and Sandved (101) who gave a more extended equation by not neglecting higher terms neglected by Debye and Hückel. These all conclude that for dilute solutions their treatments lead to the limiting law of Debye and Hückel.

Equation (XIV) may be considere an answer to those who felt that activity coefficients were nothing more than correction factors and had no physical significance. It is true that the theory only agrees with experimental results up to about 0.01 molal but the agreement over this range is good. Also, by using values for the "closest distance of approach" the theory may be extended to about 0.1 molal. For the "closest distance" of approach, "ionic radii" (102) obtained from crystal studies may be used as a first approximation. Invariably, however, a somewhat large value of a_i is required and this has been attributed to the presence of a water sheath around the ions. Actually Stokes and Robinson (103), by allowing for ion-solvent interaction as hydration, calculated on the principles of the Brunauer-Emmett-Teller adsorption isotherms (104), were able to derive an equation that reproduced observed activity coefficients to high concentrations. However, this method apparently does not work for salt mixtures (105).

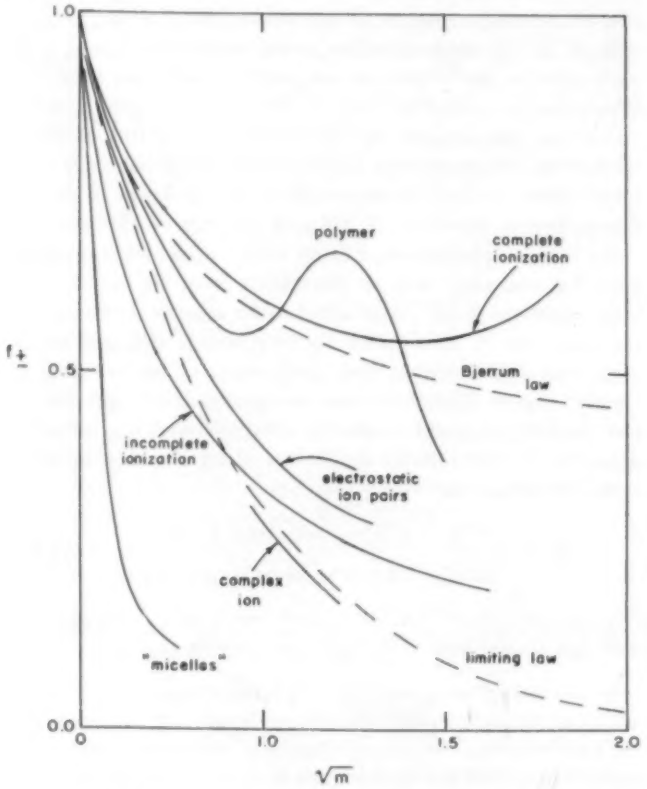


FIG. 2. Typical curves for activity coefficients of uni-univalent electrolytes in various ionic or molecular states.

Activity coefficients are also valuable in determining the state of ions in solution. In Fig. 2, several curves are shown outlining the general nature of values calculated on the premise that the solutions are totally ionized wherein values of the mean activity coefficients of uni-univalent electrolytes are plotted against the square root of the molality, m. Two dotted lines are shown: one represents the values predicted on the limiting law of Debye-Hückel wherein $a_i = 0$, the second that obtained using the Bjerrum principle wherein $a_i = 3.5$. Bjerrum's theory (106) predicts 3.5 for the lowest value that is possible without formation of "ion pairs." Results between $a_i = 0$ and $a_i = 3.5$ would therefore indicate that the solute existed in the form of "electrostatic ion pairs." Data obtained above the Bjerrum prediction would indicate complete ionization of the salt and those below the limiting law would indicate incomplete ionization of the electrolyte. Ionic "micelles" (107) give a very unique form of curve and indicate a large extent of incomplete ionization. Ions that polymerize (108) give the form of curve as depicted. Complex ions (109) as a rule fall very closely to the limiting law. Thus, the activity coefficient for $HAg(CN)_2$ falls below the limiting-law curve, $Ag(NH_3)_2Cl$ on the curve, and $Ag(NH_3)_2OH$ above the Bjerrum curve. Therefore, the last one is completely dissociated.

Debye and Hückel also applied their theory to electrolytic conductivity. The presence of an "ion atmosphere" would result in a decrease in the mobility of ions and an increase in their effective mass or a slowing down of their movement under a potential gradient, and this slowing down would become more marked the higher the solute concentration, thus accounting for the fact that equivalent conductance decreases with increased salt concentration. When a solution is subjected to a potential field the "ion atmosphere" leads to two effects. First, it will be drawn in the opposite direction to the central ion and thus slow down the movement of the central ion. Second, the ion atmosphere will tend to be drawn along with the central ion to a new location but not instantaneously. The first effect is called the electrophoretic effect, as it appears to involve movement of the solvent. The second is called the "relaxation time" effect. By statistical methods and taking care of the Brownian movement of the ions and assuming that Stokes' law applied, Onsager (17) derived the following equation for the mobility of an ion:

$$\lambda = \lambda_o - \left[\frac{0.984 \times 10^6}{(\epsilon T)^{3/2}}\,\omega\lambda_o + \frac{28.94}{(\epsilon T)^{1/2}\eta}\right]\sqrt{(z^+ + z^-)c} \qquad \text{(XVIII)}$$

where

$$\omega = z^+z^-\,\frac{2q}{1+\sqrt{q}} \qquad \text{(XIX)}$$

$$q = \frac{z^+z^-(\lambda_o^+ + \lambda^-)}{(z^+ + z^-)(z^+\lambda^- + z^-\lambda_o^+)}. \qquad \text{(XX)}$$

For the conductance of a uni-univalent electrolyte we obtain:

$$\Lambda = \Lambda_o - \left[\frac{8.20 \times 10^5}{(\epsilon T)^{3/2}}\,\Lambda_o + \frac{82.4}{(\epsilon T)^{1/2}\eta}\right]\sqrt{c} \qquad \text{(XXI)}$$

where $\Lambda_o = \lambda_o^+ + \lambda_o^-$, which may be expressed in the simple form:

$$\Lambda = \Lambda_o - (\alpha + \beta'\Lambda_o)\sqrt{c}. \qquad \text{(XXII)}$$

The Debye-Hückel-Onsager equation shows the dependency of electrolyte conductivity on concentration, temperature, viscosity, dielectric constant, and ionic valency. Their equation, therefore, served to systematize all experimental data on electrolytic conductivity. It was found, however, to be applicable only to dilute solutions or those less concentrated than about 0.01 molal. At higher concentrations, deviations from the theoretical curve are observed and are generally attributed to assumptions inherent in the Debye-Hückel-Onsager theory. Shedlovsky (110) has proposed an empirical equation applicable to about 0.1 molal.

The Onsager equation applies quite well for all media of dielectric constant exceeding 30. For media of lower dielectric constant equivalent conductances exhibit various abnormalities. Some solutions of low dielectric constant decrease in equivalent conductance on dilution instead of increasing as

normally observed, pass through a minimum and then increase on further dilution. Some exhibit both maxima and minima in their conductance curves. Walden (111) concluded that there was a definite relationship between these minima and the dielectric constant of the medium. Fuoss and Kraus (112) by an extension of the Bjerrum (106) principle were able to give a complete picture of equivalent conductance over a wide range of dielectric constant.

Bjerrum (106) using a concept of ionic association (into pairs) and the Boltzmann distribution law determined the probability of ion pair formation as a function of ionic radii. Fuoss and Kraus considered the possibility of triple-ion formation. Bjerrum and Fuoss and Kraus' concepts may be expressed by the equations:

$$A^+ + B^- \rightleftharpoons [A^+B^-]^0 \rightleftharpoons AB$$
$$[A^+B^-]^0 + A^- \rightleftharpoons [A^-B^+A^-]^- \qquad \text{(XXIII)}$$
$$[A^+B^-]^0 + B^+ \rightleftharpoons [B^+A^-B^+]^+$$

where the terms in brackets are either ion pairs or ion triplets, produced by the action of coulombic forces only. AB on the other hand would result from electronic linkage. Bjerrum concluded that all ions lying within a sphere of 3.5 Angstrom units should be considered as associated into ion pairs and all those lying beyond this sphere as "free" in the sense used by Arrhenius. His equation for the minimum ionic radius is

$$r_{min} = z_1 z_2 e^2/2\,\epsilon\,kT \qquad \text{(XXIV)}$$

where each term has the significance already given. This equation shows that the higher the dielectric constant the lower is r_{min} and therefore the less is the tendency for ion-pair formation. Bjerrum and Fuoss and Kraus derived equations for the equilibrium or rather association constants for the equations representing either ion-pair or ion-triplet formation, and for calculation of the degree or fraction of ionic association. This Bjerrum concept was used above in connection with activity coefficients (Fig. 2).

In referring to the Debye-Hückel-Onsager theory of electrolytic conductivity one might conclude that the equivalent conductances would be of higher magnitude if the effect of the ion atmosphere could in some way be eliminated or if it were not given sufficient time to form under a potential gradient. Wien (113) showed that this was true by studying the effect of high field strengths on the conductivity of electrolytes. Working at applied potentials of the order of 20,000 volts per cm he showed that the conductance increases with the field strength and approaches asymptotically a limiting value corresponding to that observed at infinite dilution, with the effect being greater the higher the valency of the ions. Also referring to the theory, if the "relaxation time" effect is eliminated one would expect the conductance to increase. Debye and Falkenhagen (114) showed that this was true by studying the effects of high frequencies on the conductance under which conditions the relaxation time effect was reduced in magnitude. The studies, therefore, of Wien and Falkenhagen presented additional evidence in confirmation of the fundamental postulates of the theory of interionic attraction on the mobility of ions. One might suspect that the Wien effect would make possible a really true determination of the degree of ionization of an electrolyte. However, when applied to weak electrolytes it was found that the high fields produced an increased ionization of the weak electrolyte, known as the "dissociation field effect" and discussed by Onsager (115). Therefore, the Wien method does not make possible a determination of a degree of dissociation in that the effect itself changes the degree of dissociation.

Electrode Reactions and Electrolytic Processes

We have seen during the past fifty years various attempts to obtain the absolute potential of a single electrode in spite of the fact that the potential of an electrode involves the activity of a single ion, a quantity thermodynamically inassessable. Most of the methods, such as the suspended-particle method, the scraped-electrode method, etc., are now conceded to be subject to errors arising from adsorption of ions or impurities at the phase boundary, the presence of oriented dipoles, or the displacement of an oriented water molecule by the electrolyte. Billiter (116) gave a review of the various methods that have been tried. That most of these lead to the same value of a reference half-cell, say the normal calomel half-cell, is in itself not significant as all of the methods are probably measuring the same phenomena at the phase boundary. It is significant, however, that some methods (117) do yield values that agree closely with the values calculated by Latimer, Pitzer, and Slansky (118) from the free energy changes for a series of changes in state which, when combined, would give the free energy change for the reaction of a single electrode. In this method, too, we must make an assumption regarding the free energy of solvation of a gaseous ion since these must either be obtained from the solvation of a molecule owing to the requirement of electroneutrality, or calculated from electrostatic relations involving an ion size.

Today we are, therefore, content to use the convention of standard electrode potentials based on the conventional hydrogen electrode and use the Nernst equation (converted to activities) to express its variation with solute activity. It is interesting that Rogers and Stehney (119) in 1949, as a result of their studies on the deposition of traces on an inert electrode, suggest that the Nernst equation should be modified to include a term to account for the energy difference in a deposit-electrode interface, or the differences obtained if an ion is deposited on the metallic state of the ion or on a dissimilar metal. They also pointed out that the Nernst complete equation rather than the abridged form should be used in all electrochemical studies relating to the deposition of traces.

In recent years the standard potential of many electrodes and oxidation-reduction reactions has been determined with higher accuracy than heretofore and by improved methods using, where possible, cells without liquid junction. It has been shown that the potential at a liquid junction between unlike solutions depends on the method used to form the junction and involves the transference numbers and activities of all the ions in the transition layer. Also for high reproducibility the junction must be maintained in an isothermal state (83, 120). Guggenheim (121) has discussed the "continuous mixture junction," the "constrained diffusion junction," the "free diffusion junction," and the "flowing junction." He concluded that each type gives reproducible results providing the transition layer meets certain theoretical considerations. Estimates of the magnitude of liquid-junction potentials may be obtained from the Henderson (122), the Planck (123), or the Pleijel (124) equations in terms of ionic concentrations and mobilities. Graphical means of evaluation may also be used (125). "True values" depend on a knowledge of individual ion activities. Since these are thermodynamically inassessible, "true" values are unobtainable. Also the converse is true: values of individual ion activities cannot be obtained from measurements of liquid-junction potentials

as such measurements depend on the way the junction is formed and include potentials at the electrode-electrolyte interfaces, also.

The electrochemical series of the elements in their standard states is essentially the same as it was at the turn of the century. Brown, Roetheli, and Forrest (126) have proposed a new electrochemical series which may be called the "corrosion potentials." This series consists of two parts: "hydrogen types" and "oxygen types." In the first type, metals are oxidized by displacing hydrogen; in the second, metals are oxidized by atmospheric oxygen diffusing into solution and to cathodic areas of the metal. The "corrosion potentials" are considered to give a more useful index of probable metallic behavior than the "standard potentials."

Our knowledge of the nonequilibrium state is not in as happy a state as our knowledge of equilibrium states. Also in many cases we use the term reversibility when strict reversibility is approached but not actually attained (127). Many theories still abound on the subjects of overvoltage, polarization, passivity, etc., and many comparisons made with the early Tafel (128) equation expressing overvoltage as a function of current density. This equation probably receives more attention than it deserves. It involves electrode area. In theorizing on the Tafel equation, probably the "true" electrode area is demanded, but in practice the "apparent" area is used. Much research on this phase of the theory of electrode processes is now under way (129). Also various "diffusion layers" and "double layers," starting with the Helmholtz (130) double layer, have been proposed to account for observed phenomena at electrodes.

In recent years, considerable attention has been given to the *theory of absolute reaction rates*. In this theory Eyring (131) and Evans and Polanyi (132) introduced the concept of the "activated complex." This theory is closely related to the Brønsted-Christiansen-Scatchard theory of reaction rates in ionic solutions wherein a "critical complex" of momentary existence forms prior to final reaction products (133–135). In essence the theory of absolute reaction rates recognizes the existence of energy barriers (diagrams with familiar valleys and peaks) over which reactants or particles must pass to form products, and the necessity that they receive a free energy of activation in order to do so. The discharge of an ion at rest, for example, involves two main energy barriers, one for the transfer of an ion from the bulk solution where it is under the influence of electrostatic forces to the surface of an electrode where it is probably free of such forces, and another for the discharge of the ion by combination with the electron supplied by the electrode. Other energy barriers associated with the orientation of the discharged ion within the lattice of the electrode or in the formation of gas bubbles are probably involved also. The actual rate is obtained from the specific rate by multiplying the latter by the activity of the reactant.

The equations used to depict these processes are the same as the one proposed in 1889 by Arrhenius (136) except that his empirical A constant is replaced by (kT/h) and his energy of activation by the free energy of activation. The factor (kT/h) was introduced by Eyring (131) as the rate of crossing the energy barrier, where k and h are, respectively, the Boltzmann and Planck constants. For any electrode process we may consider that there are two competing reactions, the forward one of discharge of an ion, and the reverse one of solution of an ion, or vice versa. Suffice it to say, that the theory of absolute reaction rates when applied to electrode processes gives the familiar Nernst equation for the equilibrium state when the two competing reactions are equal and gives an equation for the net current (assumed to be cathodic when the two rates are not equal. One form of equation (13 for the cathodic current is:

$$I = \frac{e[a_o - e^{-(E-E_o\mathfrak{F}/ET}]}{t\frac{\delta}{D} + \frac{1}{k_1}e^{-\alpha E\mathfrak{F}/RT}} \qquad \text{(XX}$$

where k_1 is the rate constant for ionic discharge, D the diffi sion coefficient of the ions, a_o the activity of the ions in th bulk of the solution, δ the thickness of the "diffusion layer, t the transference number of the ions not discharged, α th fraction of the potential E operating between the ion i solution and its activated state, E_o is the standard potenti of the electrode, and the other constants have their usu significance. This equation represents the variation of th electrode potential, E, with the current I, and it has bee included to illustrate how complicated this process is and t show how the theory of absolute reaction rates has brough together all of the factors involved at an electrode.

The theory of absolute reaction rates has been applied t the theory of overvoltage, to derivations of equations fo diffusion currents at stationary electrodes, to the theory o electrolyte diffusion, to ion transport, to rate of oxide-film formation (138), and to other problems in electrochemistry (137). Its development has been one of the highlights of th period with which we are concerned. It is true that calculation of free energies of activation still require experimental de terminations over a range of temperatures but the theory aids in correlation of data and offers much for the future.

The theory of electrolytic processes is tied very much t the theories of electrolytes and electrode reactions. In thes past years we have seen many advances in electrolytic proc esses. Probably the most outstanding new electrochemical process that resulted from theoretical considerations was th *electrolytic separation of the isotopes of hydrogen* (139). O electrolysis of water the generated gas is enriched in hydroge and the solution in deuterium. This electrolytic separation i attributed to the differences in the overvoltage of hydroge and deuterium, but other factors must enter. Greater separa tion is obtained with those metals (when used as electrodes having low hydrogen overvoltage and less separation wit those having high overvoltage. Various mechanisms have been proposed (140) for the reaction that occurs at the elec trode surface. The fact that different separation factors are obtained with different metals suggests that electrode ma terials are not as inert as frequently supposed and should be included in theories pertaining to electrode processes. Those working with galvanic cells with fused salts would be the first to concur in this viewpoint.

An important theorem dealing with the treatment of the thermodynamics of irreversibility was presented by Onsager (141) in 1931 which probably will have a profound effect on future investigations of irreversible processes in electrochemistry. His theorem is frequently referred to as the *reciprocity theorem* because he used reciprocal relations similar to those used by Thomson (142) in his treatment of thermoelectric phenomena and applied by Eastman (143) to his studies of the Soret effect in galvanic cells containing temperature gradients, by Helmholtz (144) in his studies of electrolytic cells, and by Bridgman (145) in his studies of galvanomagnetic effects in metals.

Onsager developed a general relation of reciprocity in the mutual interference of simultaneous irreversible processes

which is denied in reversible processes by the principle of microscopic reversibility. He pointed out that the thermoelectric effect arises from the mutual interference of the simultaneous irreversible processes: the flow of heat and the flow of electricity, whereby the flow of heat interferes with the flow of electricity and has a tendency to carry the electricity along with it. In other words, these two processes become entangled in their irreversibilities. He applied the theorem to transference phenomena in electrolytes and to the thermoelectric effect. Callen (146) since has applied the theorem to study of the thermomagnetic effect. Callen also used a somewhat modified approach wherein he used a theorem analogous to the Nyquist electrical noise formula and expressed the generalized resistance in a dissipative system in terms of the spectral density of the fluctuating forces of a system in equilibrium. Although the Onsager method is a highly mathematical one, it is predicted that it will be used more frequently in the future.

General Considerations

In the foregoing we have discussed the thermodynamics and electrostatic forces of electrolytes, the theory of absolute reaction rates, and a mathematical treatment of irreversibility, for which the past 50 years will be especially noted. These have or will have broad general influence in all phases of electrochemistry. One cannot help but feel, however, that during this period certain specific contributions have been made which solved once and for all certain questionable facts or problems in electrochemistry or have aided in elucidating mechanisms and which should be mentioned. With no pretense at completeness, a few will be mentioned to illustrate the role that theory has played in diversified fields of electrochemistry.

The isotopes of potassium have been separated by countercurrent electromigration (147), a method based on differences in the mobility of the isotopic ions. Isotope separations based on differences in ionic mobilities had heretofor been considered infeasible (148). The same principles were utilized to determine the current efficiency of electrodes in an environment of constant concentration rather than in varying concentrations (149) usually experienced. The mechanism of chromium deposition has been elucidated by the use of radioactive chromium (150). It was shown that chromium is deposited directly from the hexavalent state and not from the trivalent chromium present in the bath.

In 1933 Debye (151) proposed a method for the determination of the mass of electrolytic ions based on the introduction of ultrasonic waves in an electrolytic solution. Debye stated that passage of ultrasonic waves through an electrolytic solution should result in alternating potentials within the solution arising from dynamic reactions of the ions to acoustical waves. In 1949, Yeager, Bugosh, Hovorka, and McCarthy (152) for the first time detected the effect for several electrolytes, although Rutgers (153) earlier in 1946 had detected the effect for colloidal suspensions. Yeager and coauthors also showed that the effect was independent of concentration in the range 0.0005 to 0.005 molar, as predicted by Debye.

The Gladstone-Tribe (154) double-sulfate theory of the lead-acid storage battery has finally been established by analytical methods (155), thermodynamic studies (155, 156), and measurements of galvanic cells (157). Delahay, Pourbaix, and Van Rysselberghe (158) have developed potential-*p*H diagrams which give domains of corrosion, passivity, and passivation of metals in certain environments. Diagrams of this type based on thermodynamic and electrochemical data will probably become available for all metals.

We have seen the development of the "Geomagnetic Electrokinetograph" whereby the motion of the oceanic water is measured relative to the ocean's bottom, an instrument developed on theoretical considerations. The Ilkovic (159) equation has proved its merits in polarography. Several modifications of the equation have been proposed (160), but these constitute refinements in the theory rather than radical departures from the concept of Ilkovic.

Electrochemical laws governing the growth of films on metals have been enunciated (161). The theory of inhibitors of corrosion has been advanced to include structural considerations (162). Cathodic protection is well known and accepted. Elegant treatments of current density distribution in electrolytic cells have been presented (163, 164). Differential titrations (165) are recommended where high accuracy in analysis is demanded. Thermodynamics including the third law has been used to study the equilibria of Clark standard cells (166). Information on the structure of complex molecules has been supplied by electrochemical means (167, 168).

The past fifty-year period in electrochemical theory has been a fruitful and notable one. However, many problems still remain to be solved. Our treatments of concentrated solutions of electrolytes are still empirical. The problem of the potential at phase boundaries is largely unsolved. Much remains to be done in the field of electrochemical kinetics, especially if we wish to place it on a true "absolute reaction" basis. Developments in atomic energy will undoubtedly affect the direction and the progress of electrochemical research. It may well be that new advances in theoretical electrochemistry will depend on the development of newer and better mathematics. We have seen this in the past in the application of thermodynamics and statistical mechanics to electrochemical phenomena and may expect to see it repeated in the future by the applications of wave mechanics and newer mathematics. Systems will probably be treated in a somewhat different, if not more complex, fashion than at present. To those permitted to witness, the next fifty years should be most interesting.

REFERENCES

1. Michael Faraday, *Phil. Trans.*, **123**, 23 (1833); Expt. Res., 3rd Series, p. 76.
2. G. W. Vinal and S. J. Bates, *Natl. Bur. Standards Bull.*, **10**, 449 (1914).
3. E. W. Washburn and S. J. Bates, *J. Am. Chem. Soc.*, **34**, 1341 (1912).
4. F. B. Silsbee, "Establishment and Maintenance of the Electrical Units," Natl. Bur. Standards Circular 475, March 1, 1949.
5. D. N. Craig and J. I. Hoffman, "Electrochemical Constants," Natl. Bur. Standards Circular 524, in press.
6. H. Sommer and J. A. Hipple, "Electrochemical Constants," Natl. Bur. Standards Circular 524, in press.
7. J. W. M. DuMond and E. R. Cohen, "A Least-squares Adjustment of the Atomic Constants as of December 1950." A report to the National Research Council Committee on Constants and Conversion Factors of Physics, California Institute of Technology, Pasadena.
8. Svante Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).
9. Jacobus Henricus van't Hoff, *Z. physik. Chem.*, **1**, 481 (1887).
10. Wilhelm Ostwald, *Z. physik. Chem.*, **2**, 36 (1888).
11. J. Willard Gibbs, *Trans. Conn. Acad. Arts Sci.*, **2**, 309, 382 (1873); **3**, 108 (1876); *Am. J. Sci.*, **16**, 441 (1878);

18, 277, 371 (1879); *Science*, **1**, 160 (1883); *Brit. Assoc. Advancement Sci. Rep.* 388 (1886); *Nature*, **55**, 461 (1897).
12. WALTER NERNST, *Z. physik. Chem.*, **4**, 150 (1889).
13. R. M. RAOULT, *Compt. rend.*, **104**, 1430 (1887); *Z. physik. Chem.*, **2**, 353 (1888).
14. R. LORENZ, "Elektrolyse Geschmolzener Salze," Druck und Verlag von Wilhelm Knapp Halle A. Saale (1905).
15. F. KOHLRAUSCH AND A. HEYDWEILLER, *Ann. Physik.*, **53**, 209 (1894).
16. F. KOHLRAUSCH, *Ann. Physik.*, **26**, 108 (1885).
17. L. ONSAGER, *Physik. Z.*, **28**, 277 (1927); **27**, 388 (1926).
18. F. KOHLRAUSCH, L. HOLBORN, AND H. DIESELHORST, *Wied. Ann.*, **64**, 425 (1898).
19. G. JONES AND B. C. BRADSHAW, *J. Am. Chem. Soc.*, **55**, 1780 (1933).
20. L. KAHLENBERG, *Trans. Am. Electrochem. Soc.*, **1**, 121 (1902).
21. E. Q. ADAMS, *J. Am. Chem. Soc.*, **38**, 1503 (1916).
22. N. BJERRUM, *Z. physik. Chem.*, **104**, 417 (1923).
23. J. W. MCBAIN, ET AL., *J. Chem. Soc.*, **101**, 2042 (1912); **105**, 957 (1914); **113**, 825 (1918); **115**, 1300 (1919); **117**, 1506 (1920).
24. N. BRØNSTED, *Rec. trav. chim.*, **42**, 718 (1923).
25. T. M. LOWRY, *Chemistry & Industry*, **42**, 43 (1923).
26. P. DEBYE AND E. HÜCKEL, *Physik. Z.*, **24**, 185 (1923).
26a. E. GÜNTELBERG, *Z. physik. Chem.*, **123**, 199 (1926).
27. C. HERING, *Trans. Am. Electrochem. Soc.*, **13**, 273 (1908).
28. W. D. BANCROFT, *Trans. Am. Electrochem. Soc.*, **4**, 176 (1903).
29. E. F. ROEBER, *Trans. Am. Electrochem. Soc.*, **4**, 172 (1903).
30. A. A. NOYES, *Congress Arts Sci., St. Louis Exposition*, **4**, 317 (1904).
31. N. BJERRUM, *Kgl. Danske Videnskab. Selsk. Biol. Skrifter*, **4**, 1 (1906).
32. W. SUTHERLAND, *Phil. Mag.*, **7**, 1 (1906).
33. G. N. LEWIS, *Z. physik. Chem.*, **70**, 212 (1909).
34. W. H. BRAGG AND W. L. BRAGG, "X-rays and Crystal Structure," Bell Co., London, 4th ed., p. 165 (1924).
35. H. S. TAYLOR, *Trans. Am. Electrochem. Soc.*, **43**, 31 (1923).
36. E. W. WASHBURN, *Trans. Am. Electrochem. Soc.*, **21**, 125 (1912).
37. G. WIEDMANN, *Ann. Physik.*, **99**, 228 (1856).
38. W. OSTWALD, *Z. physik. Chem.*, **2**, 281 (1888).
39. P. WALDEN, *Z. physik. Chem.*, **55**, 207 (1906).
40. C. A. KRAUS AND W. C. BRAY, *J. Am. Chem. Soc.*, **35**, 1383, (1913).
41. W. NERNST, *Nachr. kgl. Ges. Wiss. Göttingen, Math-Phys. Klasse* 1 (1900).
42. H. S. TAYLOR, editor, "Treatise on Physical Chemistry," Vol. 1, 2nd ed., p. 686, D. Van Nostrand Co., Inc., New York, (1931).
43. L. G. LONGSWORTH, *J. Am. Chem. Soc.*, **69**, 1288 (1947).
44. H. S. TAYLOR, *Trans. Am. Electrochem. Soc.*, **51**, 570 (1927).
45. M. RUDOLPHI, *Z. physik. Chem.*, **17**, 385 (1895).
46. C. A. KRAUS AND W. C. BRAY, *J. Am. Chem. Soc.*, **35**, 1414 (1913); **37**, 1315 (1915).
47. B. DE SZYSZKOWSKI, *Medd. Vetenskapskad. Nobelins.*, **3**, 2 (1914).
48. S. J. BATES, *J. Am. Chem. Soc.*, **37**, 1431 (1915).
49. J. J. VAN LAAR, *Z. physik. Chem.*, **15**, 457 (1894).
50. P. HERTZ, *Ann. Physik.*, (4), **37**, 1 (1912).
51. I. C. GHOSH, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918).
52. R. MILNER, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913).
53. G. N. LEWIS, *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907); *Z. physik Chem.*, **61**, 129 (1907).
54. T. W. RICHARDS, *Z. physik Chem.*, **42**, 129 (1903).
55. W. NERNST, *Nachr. kgl. Ges. Wiss. Göttingen, Math-Phys. Klasse* 1 (1906).
56. M. PLANCK, *Ber. deut. chem. Ges.*, **45**, 5 (1912).
57. D. A. MACINNES, "The Principles of Electrochemistry," p. 131, Reinhold Publishing Corp., New York (1939).
58. N. BRØNSTED AND V. K. LAMER, *J. Am. Chem. Soc.*, **46**, 555 (1924)
59. G. SCATCHARD, P. T. JONES, AND S. S. PRENTISS, *J. Am. Chem. Soc.*, **54**, 2676 (1932), and later articles in the same journal.
60. R. P. SMITH, *J. Am. Chem. Soc.*, **61**, 497 (1939).
61. A. L. ROBINSON, *J. Am. Chem. Soc.*, **54**, 1311 (1932), and other articles in the same journal.
62. F. T. GUCKER, JR., AND K. H. SCHMINKE, *J. Am. Chem. Soc.*, **54**, 1358 (1932), and later articles in the same journal.
63. S. SHANKMAN AND A. R. GORDON, *J. Am. Chem. Soc.*, **61**, 2370 (1939).
64. H. S. HARNED AND W. J. HAMER, *J. Am. Chem. Soc.*, **57**, 27 (1935).
65. M. F. BECHTOLD AND R. F. NEWTON, *J. Am. Chem. Soc.*, **62**, 1390 (1940).
66. R. A. ROBINSON AND D. A. SINCLAIR, *J. Am. Chem. Soc.*, **56**, 1830 (1934), and later articles.
67. G. SCATCHARD, W. J. HAMER, AND S. E. WOOD, *J. Am. Chem. Soc.*, **60**, 3061 (1938).
68. R. H. STOKES, *J. Am. Chem. Soc.*, **69**, 1291 (1947).
69. H. S. HARNED AND B. B. OWEN, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York (1943).
70. Ref. (57), pp. 156–165.
71. Ref. (57), pp. 68–91.
72. G. KORTÜM AND J. O'M. BOCKRIS, "Electrochemistry," Elsevier Press, Inc., Houston, Texas (1951).
73. D. A. MACINNES AND T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1429 (1932).
74. Ref. (69), chap. 15
75. J. A. BEATTIE, *J. Am. Chem. Soc.*, **46**, 2211 (1924).
76. H. S. HARNED AND W. J. HAMER, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
77. W. J. HAMER, unpublished calculations; data of H. S. HARNED and N. D. EMBREE, *J. Am. Chem. Soc.*, **56**, 1042 (1934) used.
78. L. F. NIMS, *J. Am. Chem. Soc.*, **56**, 1110 (1934).
79. H. S. HARNED AND N. D. EMBREE, *J. Am. Chem. Soc.*, **56**, 1050 (1934).
80. S. P. L. SØRENSEN, *Compt. rend. Lab. Carlsberg*, **8**, 1 (1909).
81. D. I. HITCHCOCK AND A. C. TAYLOR, *J. Am. Chem. Soc.*, **59**, 1812 (1937).
82. D. A. MACINNES, D. BELCHER, AND T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **60**, 1094 (1938).
83. W. J. HAMER, *Trans. Electrochem. Soc.*, **72**, 45 (1937).
84. W. J. HAMER AND S. F. ACREE, *J. Research Natl. Bur. Standards*, **23**, 647 (1939).
85. E. A. GUGGENHEIM, *J. Phys. Chem.*, **34**, 1758 (1930).
86. D. I. HITCHCOCK, *J. Am. Chem. Soc.*, **58**, 855 (1936).
87. W. J. HAMER, G. D. PINCHING, AND S. F. ACREE, *J. Research Natl. Bur. Standards*, **36**, 47 (1946).
88. W. J. HAMER AND S. F. ACREE, *J. Research Natl. Bur. Standards*, **32**, 215 (1944).
89. H. S. HARNED, *J. Am. Chem. Soc.*, **48**, 326 (1936); H. S. TAYLOR, "Treatise on Physical Chemistry," 2nd ed., Vol. I, p. 803, D. Van Nostrand Co., Inc., New York (1930).
90. E. A. GUGGENHEIM, *J. Phys. Chem.*, **34**, 1758 (1930).
91. Ref. (88), p. 222.
92. W. M. CLARK AND H. A. LUBS, *J. Biol. Chem.*, **25**, 479 (1916).
93. Brit. Standard 1647, "*p*H Scale," British Standards Inst., London (1950).
94. W. J. HAMER, *J. Wash. Acad. Sci.*, **29**, 551 (1939).
95. W. J. HAMER, unpublished calculations.
96. G. N. LEWIS AND M. RANDALL, *J. Am. Chem. Soc.*, **43**, 1112 (1921).
97. E. HÜCKEL, *Physik. Z.*, **26**, 93 (1925).
98. H. A. KRAMERS, *Proc. Acad. Sci. Amsterdam*, **30**, 145 (1927).

R. H. Fowler, *Trans. Faraday Soc.*, **23**, 434 (1927).
J. G. Kirkwood, *J. Chem. Phys.*, **2**, 767 (1934).
T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1928).
L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927).
R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, 70, 870 (1948).
S. Brunauer, P. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
R. A. Robinson, private communication.
N. Bjerrum, *Kgl. Danske Videnskab. Selsk. Math.-fys. Medd.*, **1**, 1 (1926).
J. W. McBain and M. D. Betz, *J. Am. Chem. Soc.*, **57**, 1909 (1935).
E. R. B. Smith and R. A. Robinson, *Trans. Faraday Soc.*, **38**, 70 (1942).
M. Randall and J. O. Halford, *J. Am. Chem. Soc.*, **52**, 178 (1930).
T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).
P. Walden, *Z. physik. Chem.*, **94**, 263 (1920); **100**, 512 (1922).
R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 21 (1933).
M. Wien, *Ann. Physik*, **83**, 327 (1927); *Physik. Z.*, **28**, 834 (1927).
P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).
L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).
J. Billiter, *Trans. Electrochem. Soc.*, **57**, 351 (1930).
D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).
W. M. Latimer, K. S. Pitzer, and C. M. Slanksy, *J. Chem. Phys.*, **7**, 108 (1939).
L. B. Rogers and A. F. Stehney, *J. (and Trans.) Electrochem. Soc.*, **95**, 25 (1949).
W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 662 (1935).
E. A. Guggenheim, *J. Am. Chem. Soc.*, **52**, 1315 (1930).
P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907).
M. Planck, *Z. physik. Chem.*, **39**, 161 (1890); **40**, 561 (1890).
H. Pleijel, *Z. physik. Chem.*, **72**, 1 (1910).
D. A. MacInnes and L. G. Longsworth, *Cold Spring Harbor Symposia Quant. Biol.*, **4**, 18 (1936).
R. H. Brown, B. E. Roetheli, and H. O. Forrest, *Ind. Eng. Chem.*, **23**, 350 (1931).
R. E. Kirk and D. F. Othmer, Editors, "Encyclopedia of Chemical Technology," Vol. 3, p. 292, The Interscience Encyclopedia, Inc., New York (1949).
J. Tafel, *Z. physik. Chem.*, **50**, 641 (1904).
Symposium on Polarization, Anniversary Meeting of Electrochemical Society, Philadelphia, Pa., May 1952.
H. V. Helmholtz, *Wied. Ann.*, **7**, 337 (1879).
H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); *Chem. Revs.*, **17**, 65 (1935).
M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1925); **33**, 448 (1937).
N. Brønsted, *Chem. Revs.*, **5**, 231 (1928).
J. A. Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).
G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).
S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1899).
S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chap. X, McGraw-Hill Book Co., New York (1941).
E. A. Gulbransen, *Trans. Electrochem. Soc.*, **83**, 301 (1943).
E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci. U. S.*, **18**, 496 (1932).
A. Frumkin, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **37**, 473 (1940).
L. Onsager, *Phys. Rev.*, **37**, 405 (1931).
W. Thomson (Lord Kelvin), *Trans Proc. Roy. Soc. Edinburgh*, **21**, 123 (1857); Collected Papers, **1**, 237–41 (1882).
E. D. Eastman, *J. Am. Chem. Soc.*, **48**, 1482 (1926); **50**, 283, 292 (1928).
H. V. Helmholtz, *Wied. Ann.*, **3**, 201 (1876); *Wiss. Abh.*, **1**, 840 (1877).
P. W. Bridgman, "Thermodynamics of Electrical Phenomena in Metals," The Macmillan Company, New York (1934).
H. B. Callen, *Phys. Rev.*, **73**, 1349 (1948).
A. K. Brewer, S. Madorsky, and J. W. Westhaver, *Science*, **104**, 156 (1946).
J. Kendall and E. C. Crittenden, *Proc. Nat. Acad. Sci. U. S.*, **9**, 75 (1923).
W. J. Hamer, *J. Research Natl. Bur. Standards*, **39**, 141 (1947).
F. Ogburn and A. Brenner, *J. (and Trans.) Electrochem. Soc.*, **96**, 347 (1949).
P. Debye, *J. Chem. Phys.*, **1**, 13 (1933).
E. Yeager, J. Bugosh, F. Hovorka, and J. McCarthy, *J. Chem. Phys.*, **17**, 411 (1949).
A. J. Rutgers, *Physica*, **5**, 46 (1938); *Nature*, **157**, 74 (1946).
J. H. Gladstone and A. Tribe, *Nature*, **25**, 221, 461 (1882); *Electrician*, **9**, 612 (1882).
G. W. Vinal and D. N. Craig, *J. Research Natl. Bur. Standards*, **14**, 449 (1935).
D. N. Craig and G. W. Vinal, *J. Research Natl. Bur. Standards*, **24**, 475 (1940).
H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 33 (1935).
P. Delahay, M. Pourbaix, and P. Van Rysselberghe, *J. Electrochem. Soc.*, **98**, 57, 65 (1951).
D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934); **10**, 249 (1938); *J. Chem. Phys.*, **35**, 129 (1938).
O. H. Müller, "Electrochemical Constants," Natl. Bur. Standards Circular 524, in press.
U. R. Evans, *Trans. Electrochem. Soc.*, **83**, 335 (1943).
C. A. Mann, *Trans. Electrochem. Soc.*, **69**, 115 (1936).
C. Kasper, *Trans. Electrochem. Soc.*, **77**, 353, 365 (1940); **78**, 131, 147 (1940); **82**, 153 (1942).
C. Wagner, *J. Electrochem. Soc.*, **98**, 116 (1951).
D. A. MacInnes and P. T. Jones, *J. Am. Chem. Soc.*, **48**, 2831 (1926), and later articles in the same journal.
W. F. Giauque, R. E. Barieau, and J. E. Kunzler, *J. Am. Chem. Soc.*, **72**, 5685 (1950).
E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York (1943).
Ann. N. Y. Acad. Sci., **41**, Art. 4, 241–328 (1941).

REVIEW OF ELECTROCHEMISTRY OF GASES[1]

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Examination of any treatise of electrochemistry shows that the chemical behavior of gases in electrical discharge has been more retarded in development or neglected than any other recognized branch of electrochemistry. Perhaps it would not be out of place in beginning this review to examine the several causes of this neglect and to see what future, if any, one may expect for the application of electrical energy to gases.

One naturally thinks of a comparison with the electrolysis of electrolytes but soon sees that there is little parallel between the two. In an electrolyte, ionization occurs spontaneously by action of the forces between solvent and solute and without the application of any external field. A low voltage is then sufficient to separate the products of electrolysis at the electrodes. The flow of current will, of course, obey Ohm's law. The resistance will depend on electrode separation, on the concentration, and on the conductance of the electrolyte which, in turn, depends on the mobility of the positive and negative ions. All of this is well known but does not mean that all the phenomena of electrolysis are equally well understood. What happens to ions arriving at the electrode before they react in deposition of metal, evolution of gas, or equivalent oxidation or reduction in accordance with Coulomb's law remains obscure. The role of free radicals is not well understood.

In electrical discharge in gases, the principles are entirely different. Relatively high voltage must be applied to accelerate electrons from the electrode to a velocity at which they can ionize the gas molecules encountered, thus making continuous discharge possible. The resulting chemical reaction takes place in the gas phase, not at the electrode, as in electrolysis, and may be due to direct action upon recombination of the ions or to free radicals or to both. The radicals or free atoms may be produced by direct action of the electron encounters, or by subsequent dissociation of the ion, or by excitation either with or without collision.

The potentials that electrons must attain in order to produce either ionization or excitation are considerably higher than the energies of activation of thermal chemical reactions. This means that energy-wise the production of chemical action in electrical discharge in gases may not be favorable.

What is the situation in current efficiency? What of Coulomb's law, the limiting factor in all electrolysis? In gases there is no such relation. Since the reaction takes place by recombination of ions in the gas phase or by the action of uncharged free radicals the current carried does not follow Coulomb's law in the least. And here is a factor favorable to the electrochemistry of gases; since the number of ions reacting, directly or indirectly, in the gas phase far exceeds the number conducting current by discharge at the electrode, chemical production far exceeds Coulomb equivalence. In some cases less than 100 coulombs is required instead of the 96,500 of electrolysis. But in spite of the favorable current yield the voltage necessary for continued discharge in gases is so much higher than that in electrolysis that the energy yield generally remains quite unfavorable for gaseous discharge.

Of course the voltage required for gaseous discharge may be lowered by reducing the gas pressure but this gains nothing in production since it simply makes it easier for electrons to pass without colliding with the gas molecules. But collisions are necessary for chemical activation, whatever its character.

The oldest electrochemical process in gaseous discharge, and one of the few to attain any industrial application, is the fixation of nitrogen and oxygen in air by the arc process. This reaction is generally regarded as thermal rather than electrical, though there are some recent claims that ions also play a role. Owing to its high cost, except when electrical power is very cheap, the arc process has been replaced by the catalytic ammonia synthesis. A return toward thermal synthesis in air is indicated by application of the regenerative Royster stove now being perfected by Dr. Farrington Daniels.

Another application of electrical discharge in gases is ozone production in air or oxygen. A condenser type of discharge is usually employed in the well-known "ozonizer" type of equipment. Electrical discharge is the most efficacious method of producing ozone, the application of which is limited only by the need for ozone which has had a rather "on and off" history. It is rather surprising that this isomer of oxygen, so unique in its properties and easily produced has not found larger uses. The production of organic ozonides is usually confined to organic research, the small needs of which are simply met by laboratory ozonizers. The principal application of ozone as disinfectant has been in water purification and in the sterilization of food products and grains. These uses appear to be increasing and there have recently been accounts of installations of equipment to produce ozone in ton quantities by improved equipment.

The ion efficiency of ozone production has been studied by the action of alpha rays on oxygen. These researches have shown that ozone is decomposed by the same reagents that cause its formation. The most favorable yield will then be attained when the ozone formed is most quickly withdrawn from the field of action.

The chemical action of electrical discharge on gases is by no means a new subject of investigation. More than a century ago, as soon as suitable sources of electrical power became available many gaseous reactions were studied in silent or spark discharge, especially by French chemists. The fact that none of the reactions studied have led to practical application is explained by the unfavorable energy yield already discussed.

Another unfavorable factor is the diversity of products obtained. This is especially true in the hydrocarbon gases, which react readily in electrical discharge, but owing to secondary and simultaneous reactions the mixture of products is exceedingly complex.

These difficulties have not deterred E. P. Schoch of the University of Texas from seeking to beneficiate natural gas by subjecting it to electrical discharge, using novel and ingenious equipment. Schoch early found glow discharge to be the most advantageous type of electrical discharge for chemical production. In seeking to overcome the disadvantages of low gas pressure, already mentioned, he made the important discovery that glow discharge can be maintained at higher pressures (atmospheric or somewhat above) if the rate of gas flow be increased accordingly. He found an empirical formula applicable to methane: gas flow per kwhr =

[1] For more extensive review of this subject see References (1) and (2).

[2] Carbide & Carbon Chemicals Company, Oak Ridge, Tennessee.

$Fo \times p^{1.6}$ and proved experimentally that with values of Fo greater than 1.09, the discharge has the character of a glow, and with values of Fo less than 0.656, the character of an arc. Fo is the rate of flow in ft³/kwhr and p is the pressure in cm of Hg.

Professor Schoch's first objective has been the conversion of methane to acetylene (3). This he has done by feeding the gas through a manifold electrode revolving rapidly past a stationary outer circular terminal. The objects of this procedure are to maintain turbulence and to remove the product of reaction from the field of discharge before it undergoes secondary action. The same technique is applicable to other gas reactions.

Schoch also reports the recapture of the high energy of ion recombination to increase the yield of product sought. This conservation of energy appears so essential as to indicate further detailed study.

Carbon black is a valuable by-product in producing acetylene by electrical discharge. Other applications are also being considered by Schoch; for example, the production of aromatic liquids from natural gas, of hydrogen peroxide from water vapor, and of benzene, olefines, or higher paraffines from methane. By his ingenious method, Professor Schoch has brought his costs at least to the border line of possible economic competition and has admirably demonstrated the possibilities of electrical discharge in gases and the desirability of further research. In evaluating Schoch's accomplishments, one should not overlook the fact that economically he has had to compete with the rising cost of natural gas from the time when it used to be burned to get rid of it until its present extension as fuel in the ever-widening system of pipelines across the country.

Although discharge in liquids to produce chemical action does not fall within the title of this review, in hydrocarbons, at least, the reactions are so similar they cannot properly be omitted. By elimination of hydrogen or methane, hydrocarbons condense to products of higher molecular weight and viscosity. In Germany oils of low viscosity have been converted to lubricating grade by passing discharge through thin, continuously renewed layers until the desired viscosity is attained.

The future of the electrochemistry of gases presents a challenge equally perplexing to theoretical approach and to practical application. Despite the wealth of experimental results and products which it offers, it has for more than a century resisted the modern progress of applied science and engineering. One is left still seeking the pot of gold at the end of the rainbow.

REFERENCES

1. G. Glockler and S. C. Lind, "Electrochemistry of Gases and of Other Dielectrics," John Wiley & Sons, Inc., New York (1939).
2. Irving A. Breger, "Effects of Electrical Discharge and Radiation on Organic Compounds," reprint from Report of Progress of Petroleum Research, American Petroleum Institute (1946–47).
3. *Univ. Texas Publ. Number 5011* (1950) and private communications.

THE ELECTROCHEMISTRY OF IONIC CRYSTALS[1]

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Introduction

In recent years the electrical properties of solid halides, oxides, and sulfides have been widely investigated, particularly because these substances are used industrially in rectifiers and photocells, as phosphors, and for other purposes. In many cases, the electrical conductivity depends not only on temperature but also on small deviations from the ideal stoichiometric ratio of metal to nonmetal, the presence of foreign substances in small concentrations, and eventually on grain size and previous heat treatment. By and large, reproducible results can be obtained only if the significant chemical factors are adequately defined. Thus, the "electrochemistry" of ionic crystals has become an important topic of present research.

There are characteristic differences between the electrochemistry of aqueous solutions and the electrochemistry of ionic crystals, but still more remarkable seems the fact that there are basic problems which can be treated by analogy. This is especially true with systems involving predominant ionic conduction.

In the following, the analogies between problems of aqueous solutions and those of ionic crystals are stressed, in particular since the author has widely used such analogies in addition to concepts borrowed from physics and crystallography.

Ionic and Electronic Conduction

Between ionic and electronic conduction one may distinguish in the following way. The passage of an electrical current necessarily leads to an electrochemical reaction at the boundary between a metal involving electronic conduction and an ionic conductor such as AgI. At a "cathode" where electrons and positively charged metal ions migrating in opposite directions encounter each other, metal is deposited, e.g., $Ag^+ + e^- = Ag$. Conversely, at an "anode," either metal is dissolved, or nonmetal such as chlorine is developed.

The validity of Faraday's law for solid conductors was first shown by Warburg and Tegetmeier (1), Haber and Tolloczko (2), and Bruni and Scarpa (3). Later Tubandt and associates (4–9) conducted systematic investigations. In particular, they have shown that Faraday's law holds with an accuracy better than 0.1 per cent in the case of the silver halides (AgCl, AgBr, AgI).

Moreover, Tubandt (7) has shown that in the silver halides practically only cations are mobile. As indicated in Fig. 1 the weight changes of AgI pellets between silver electrodes were determined after a known amount of coulombs had been passed. The silver anode decreased its weight in accordance with Faraday's law corresponding to the electrochemical reaction Ag (metal) = Ag^+ (in AgI) + e^- (in Ag). The weight of the AgI pellets 1 to 3, which could easily be separated from each other, was found to have remained constant. AgI pellet 4 could not be separated from the adjacent cathodic silver cylinder. The weight increase of the latter combination equalled the weight loss of the anode. The constancy of the weight of AgI pellets 1 to 3 indicates that practically only silver ions migrate (with respect to the boundaries between adjacent AgI pellets as reference planes). But iodine ions practically do not migrate, since iodine ions eventually arriving at the anode and reacting with silver ions originating from the anode would lead to a weight increase of AgI pellet 4.

On the other hand, $PbCl_2$, $PbBr_2$, $BaCl_2$, and $BaBr_2$ exhibit practically only anionic conduction (6, 7, 9).

"Mixed conduction" through both cations and anions in comparable amounts is found in the alkali halides and PbI_2 (9).

In contradistinction to the aforementioned substances there is practically no electrochemical reaction at the boundary Cu/Cu_2O below 600°C. The same is true with many other oxides and sulfides. In these substances, conduction is due preponderately to the migration of electrons.

Precise measurements, however, show that at 1000°C there is a fraction of about 0.05 per cent cationic conduction in Cu_2O (10, 11). The same is true for other oxides and sulfides, e.g., Ag_2S (12, 13).

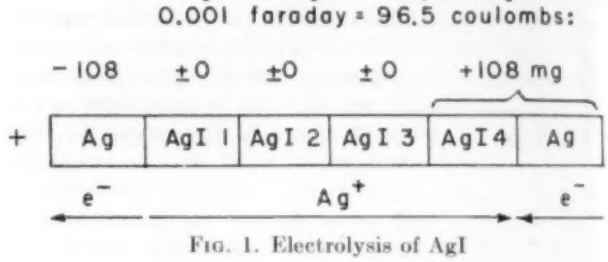

FIG. 1. Electrolysis of AgI

Small deviations from the ideal stoichiometric ratio of metal to nonmetal may affect the ratio of ionic to total conductivity to a large extent as has been shown especially in the case of the monovalent cuprous halides (6, 14–16).

The Mechanism of Ionic Conduction

Frenkel (17) has suggested the following interpretation for cationic conduction in AgCl and AgBr. In a state of thermodynamic equilibrium, some silver ions do not occupy proper lattice sites but interstitial sites as is shown in Fig. 2. This is the so-called Frenkel disorder type. Silver ions on interstitial sites may jump to adjacent interstitial sites. A silver ion on an interstitial site may also push an adjacent silver ion on a normal lattice site to an interstitial lattice site as is indicated on the right-hand side of Fig. 2. In addition, a silver ion on a normal lattice site may move to an adjacent cation vacancy, indicated by a square in Fig. 2, whereby a cation vacancy is created at the original position of the migrating silver ion. In this way, both cations on interstitial positions and cation vacancies contribute to the electrical conductivity. In principle, anions on interstitial sites and anion vacancies will also be present. Since the fraction of anionic conductivity is less than 0.1 per cent, the concentration of anion defects may tentatively be assumed to be small in comparison to the concentration of cation defects.

Extreme cases of the Frenkel disorder type occur in the high temperature modifications of AgI, Ag_2S, Cu_2S, and Ag_2HgI_4, in which compounds the cations are distributed essentially at random on a relatively large number of nearly equivalent sites, whereas the anions form a normal well-

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ordered structure as has been found by means of x-ray investigations (18–20).

In alkali halides, both cations and anions contribute to electrical conduction. Consequently, there must be mobile cations and anions as well, i.e., either interstitial ions and/or vacancies. Schottky (21) has shown theoretically that interstitial cations and anions are rare in view of the high energy required for their formation. As a limiting case, one has the so-called Schottky disorder type with only cation and anion vacancies in equivalent concentrations, which is shown in Fig. 3.

Other theoretical limiting cases are: (*a*) the anti-Frenkel disorder type with interstitial anions and anion vacancies in equal concentrations, and (*b*) the anti-Schottky disorder type with interstitial cations and anions in equivalent concentrations.

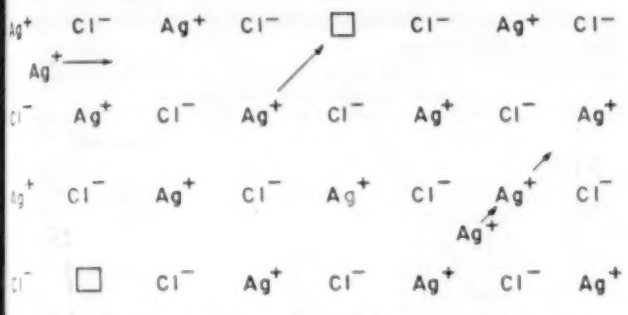

FIG. 2. Lattice defects in AgCl (Frenkel disorder type)

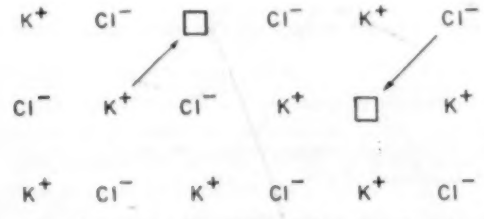

FIG. 3. Lattice defects in KCl (Schottky disorder type)

As a superordinate concept for interstitial ions and vacancies one may use the term "lattice defect." The relative preponderance of certain lattice defects is determined essentially by the energy changes accompanying the formation of the various pairs of lattice defects from an ideal crystal as has been discussed by Schottky (21) and Jost and Nehlep (22). Calculations for the formation of vacancies in alkali halides have been refined by Mott and Littleton (23) and Hutner, du Pré, and Rittner (24).

The Degree of Disorder in Silver Halides and Alkali Halides

Koch and Wagner (25) have shown how one may determine the concentrations of the various lattice defects in a given salt from measurements of the electrical conductivity, transference numbers, lattice parameters, and pyknometric densities of the pure salt and solid solutions involving additives with different cation/anion ratios, e.g., $CdBr_2$ or Ag_2S in AgBr.

The thermodynamic equilibrium between interstitial cations, cation vacancies, and silver ions on normal lattice positions, may be treated as an analogue to the equilibrium

$$2\,H_2O = H_3O^+ + OH^- \qquad (I)$$

in aqueous solutions where H_3O^+ ions may be considered as "protons on interstitial sites" and OH^- ions as "proton vacancies." Apart from the migration of H_3O^+ and OH^- ions, electrical conduction is due to proton transfer between H_3O^+ ions and H_2O molecules and between OH^- ions and H_2O molecules, respectively.

In aqueous solutions, one has the well-known equilibrium condition

$$c_{H_3O^+} \times c_{HO^-} = K_w \qquad (II)$$

where the symbol c denotes concentrations in mole/cm³. In pure water, i.e., if no other ions are present, the concentrations of H_3O^+ and OH^- ions must be equal according to the stoichiometric equation (I). Thus

$$\mathring{c}_{H_3O^+} = \mathring{c}_{OH^-} = K_w^{\frac{1}{2}} \qquad (III)$$

where the degree superscript sign is used in order to denote concentrations in pure water.

As an analogue to equation (I), one has for solid AgCl or AgBr

$$Ag^+ \text{ on normal lattice site} = Ag^+ \text{ on interstitial site} + Ag^+ \text{ vacancy.} \qquad (IV)$$

Assuming the validity of the laws for ideal dilute solutions, one has the equilibrium condition

$$c_{\bigcirc} \times c_{\square} = K \qquad (V)$$

where $c_{\bigcirc}$ and $c_{\square}$ are the concentrations of Ag^+ ions on interstitial sites and Ag^+ vacancies, respectively. Equation (V) is an analogue to equation (II). In pure AgCl or AgBr the concentration of interstitial cations must equal the concentration of cation vacancies if no other lattice defects are present. Thus

$$\mathring{c}_{\bigcirc} = \mathring{c}_{\square} = K^{\frac{1}{2}}. \qquad (VI)$$

The ratio of the number of interstitial cations or cation vacancies to the total number of cations has been designated as the "degree of disorder" α as an analogue to the degree of dissociation in aqueous solutions. Both values may be obtained from conductivity measurements. The electrical conductivity of pure water may be expressed as

$$\kappa^\circ(H_2O) = \mathbf{F}(\mathring{c}_{H_3O^+} \times u_{H_3O^+} + \mathring{c}_{OH^-} \times u_{OH^-}) \qquad (VII)$$

where $\mathbf{F}$ is the Faraday constant and $u_{H_3O^+}$ and u_{OH^-} are the mobilities which also include the contribution of proton transfer. The mobilities may be derived from measurements of the electrical conductivity of solutions with known concentrations of these ions. For instance, the electrical conductivity of a dilute solution of hydrogen chloride of concentration c_{HCl} equals

$$\kappa(HCl \text{ in } H_2O) = \mathbf{F}(u_{H_3O^+} + u_{Cl^-})c_{HCl}. \qquad (VIII)$$

Hence it follows that

$$u_{H_3O^+} = t_{H_3O^+(HCl)} \times \kappa(HCl \text{ in } H_2O)/(\mathbf{F}c_{HCl} \qquad (IX)$$

where $t_{H_3O^+(HCl)}$ is the transference number of H_3O^+ ions in a dilute HCl solution. Similarly, the mobility of OH^- may be derived from the electrical conductivity of dilute NaOH solutions. Then one obtains from equation (VII) the following equation used first by Kohlrausch and Heydweiller (26)

$$\mathring{c}_{H_3O^+} = \mathring{c}_{OH^-} = \kappa(H_2O)/[\mathbf{F}(u_{H_3O^+} + u_{OH^-})]. \qquad (X)$$

In the case of solid salts, one may proceed in a similar fashion in order to obtain the concentration of lattice defects as has been shown, e.g., for AgBr by Koch and Wagner (25)

and Teltow (27). The electrical conductivity of pure silver bromide may be expressed as

$$\kappa^{\circ}(\mathrm{AgBr}) = \mathbf{F}(c_{\bigcirc}^{\circ}u_{\bigcirc} + c_{\square}^{\circ}u_{\square}) \qquad \text{(XI)}$$

where $u_{\bigcirc}$ and $u_{\square}$ are the mobilities of silver ions on interstitial sites and cation vacancies, respectively.

The mobility of cation vacancies, $u_{\square}$, is to be derived from measurements of the conductivity of solutions involving known concentrations of cation vacancies. Such solutions are, e.g., solid solutions of $PbBr_2$ or $CdBr_2$ in AgBr. Since in $CdBr_2$ the cation/anion ratio is 1/2 instead of 1/1 in AgBr, a solid solution of $CdBr_2$ in AgBr is possible only if there are excess anions on interstitial sites, or a cation vacancy for each deficit cation. In view of the large size of the anions, only the latter possibility is to be considered (Fig. 4). According to the equilibrium condition in equation (VI), the concentration of

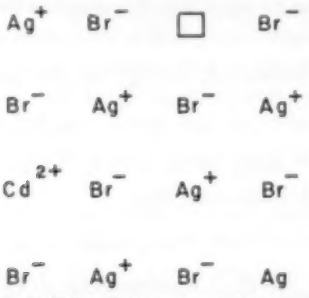

FIG. 4. Solid solution in AgBr + $CdBr_2$

cation vacancies is increased. Since the crystal as a whole must be electrically neutral, one has

$$c_{\mathrm{Cd}^{++}\bullet} + c_{\bigcirc} = c_{\square} \qquad \text{(XII)}$$

where $c_{\mathrm{Cd}^{++}\bullet}$ is the symbol of a cadmium ion substituted for a silver ion. For sufficiently high concentrations of $CdBr_2$ in AgBr, one may disregard the presence of interstitial silver ions and thus obtains for the conductivity of a solid solution of $CdBr_2$ in AgBr

$$\begin{aligned}\kappa(\mathrm{CdBr_2\ in\ AgBr}) &\cong \mathbf{F}u_{\square}c_{\square} \\ &\cong \mathbf{F}u_{\square}c_{\mathrm{Cd}^{++}\bullet} \qquad \text{if } c_{\square} \gg c_{\bigcirc}.\end{aligned} \qquad \text{(XIII)}$$

In accordance with equation (XIII) it has been found that the electrical conductivity of a solution of $CdBr_2$ in solid AgBr is nearly proportional to the $CdBr_2$ content in a rather wide concentration range, e.g., between 0.2 and 4 molar per cent at 250°C. Thus the mobility of silver ion vacancies may be calculated as

$$u_{\square} = \kappa(\mathrm{CdBr_2\ in\ AgBr})/(\mathbf{F}c_{\mathrm{Cd}^{++}\bullet}). \qquad \text{(XIV)}$$

In principle, it should be possible to obtain the mobility of interstitial silver ions in a similar fashion from the conductivity of solid solutions of Ag_2S in AgBr involving excess cations. Teltow (28) has shown that in fact the presence of Ag_2S increases the electrical conductivity of AgBr (up to 50 per cent at 175°C). Unfortunately, however, the solubility of Ag_2S in silver halides is so small that one cannot prepare solutions in which $c_{\bigcirc} \gg c_{\square}$. Therefore one cannot obtain directly the value of $u_{\bigcirc}$.

The right-hand side of Fig. 5 shows a minimum of the electrical conductivity of AgBr at rather low concentrations of $CdBr_2$. In this range the increase in the concentration of cation vacancies nearly equals the decrease in the concentration of interstitial cations. The minimum in Fig. 5 therefore indicates that the mobility of interstitial cations is higher than that of cation vacancies (25). A quantitative analysis of the plot in Fig. 5 yields the ratio $u_{\bigcirc}/u_{\square}$ (27). Therefrom one may also calculate the value of $u_{\bigcirc}$.

Hence one has

$$c_{\bigcirc}^{\circ} = c_{\square}^{\circ} = \kappa^{\circ}(\mathrm{AgBr})/[\mathbf{F}(u_{\bigcirc} + u_{\square})] \qquad \text{(XV)}$$

as an analogue to equation (X). Subsequently one may calculate the degree of disorder defined above.

This procedure presupposes the validity of the laws of ideal dilute solutions, and therefore is applicable only to systems with rather low concentrations of lattice defects and additives. At higher concentrations there are the same complications as in aqueous solutions, viz., electrostatic interaction and association. From a theoretical point of view, the evaluation of experiments involving low concentrations is most desirable. However, the lower the concentrations of lattice defects and additives, the less reliable are the experimental values because of the presence of unknown impurities and other difficulties.

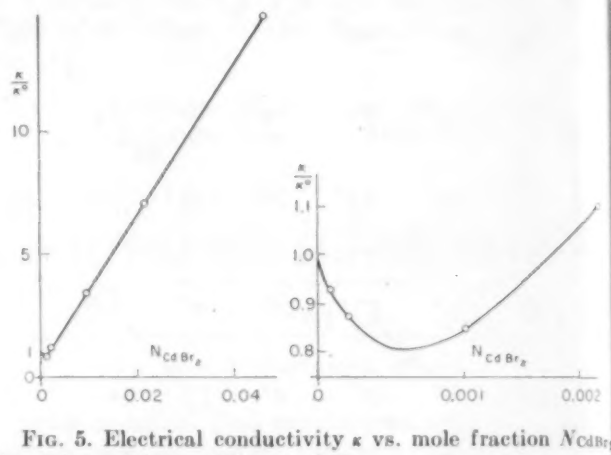

FIG. 5. Electrical conductivity κ vs. mole fraction N_{CdBr_2} for solid solutions AgBr + $CdBr_2$.

Consequently, results for higher concentrations have to be used after corrections for deviations from the limiting laws for dilute solutions have been provided. These corrections cannot be calculated with a high degree of accuracy but may be estimated within certain limits. Results obtained in this way by Teltow (27) are compiled in Table I.

If in equation (VI) for pure silver bromide the concentration of cations on interstitial sites is set equal to the concentration of cation vacancies, it is implied that the concentration of anion vacancies is negligible, i.e., is less than ten per cent of the concentration of cation vacancies. This assumption is in accordance with the results of determinations of the pyknometric density and the lattice parameter from x-ray investigations (29, 30) and with measurements of the pressure dependence of the electrical conductivity of AgBr (31, 32). On the other hand, the assumption of the Schottky disorder type suggested for AgBr by Mitchell (33) is in conflict with the aforementioned results, with the increase of the electrical conductivity of AgBr by addition of Ag_2S (28), and with the existence of a minimum of the conductivity of solid solutions of $CdBr_2$ in AgBr as a function of the AgBr content (25, 27). The existence of anion vacancies has been shown qualitatively by a finite diffusion rate of sulfur ions in AgBr (28) and by optical observations on solid solutions of Ag_2S in AgBr according to Stasiw (34). Thus, the concentration of anion vacancies in AgBr at 250° to 400°C may be between 0.01 and 10 per cent of the concentration of cation vacancies.

Kelting and Witt (35), Wagner and Hantelmann (36), Etzel

and Maurer (37), and Haven (38) have conducted analogous investigations on KCl, NaCl, and the lithium halides. These experiments have been evaluated under the assumption that virtually only cation and anion vacancies are present. The mathematical relations are essentially of the same type as those for silver halides, but quantities referring to anion vacancies appear instead of those referring to interstitial cations. Results for KCl are compiled in Table II.

TABLE I. *Degree of disorder α in solid* AgBr *according to Teltow* (27)

Temperature (°C)	α
200	0.7×10^{-4}
225	1.5×10^{-4}
250	3.4×10^{-4}
275	6.9×10^{-4}

TABLE II. *Degree of disorder α in solid* KCl *according to Wagner and Hantelmann* (36)

Temperature (°C)	α
600	0.8×10^{-5}
625	1.2×10^{-5}
650	2.1×10^{-5}
675	3.0×10^{-5}
700	4.1×10^{-5}
725	5.7×10^{-5}

Solid Solutions with Anionic Conduction

According to Croatto and Bruno (39) the ionic conductivity of SrF_2 is increased by dissolution of LaF_3 owing to the presence of F^- ions on interstitial sites. On the other hand, ionic conduction in the oxides of tetravalent metals with oxides of trivalent metals as solutes ($CeO_2 + La_2O_3$; $ZrO_2 + Y_2O_3$) is due to anion vacancies (40). Conduction via anion vacancies also accounts for the increase of the electrical conductivity of $PbCl_2$ caused by small amounts of KCl or AgCl (41–45).

Solubility Problems

In the case of aqueous solutions, the concept of electrolytic dissociation of the solvent and dissolved substances has far-reaching consequences apart from electrochemical problems. For instance, in a solution saturated with thallium hydroxide, involving the equilibrium

$$TlOH\ (cr) = Tl^+ + OH^-, \qquad (XVI)$$

the product of the concentrations of Tl^+ and OH^- ions is equal to a constant called solubility product,

$$c_{Tl^+} \times c_{OH^-} = L_{TlOH}. \qquad (XVII)$$

Consequently, the concentration of thallium ions in a solution saturated with thallium hydroxide is decreased by adding another electrolyte furnishing OH^- ions, e.g., sodium hydroxide.

The stoichiometric equation for the dissolution of $PbCl_2$ in solid AgCl reads

$$PbCl_2(cr) = Pb^{2+}\bullet + \text{cation vacancy} + 2Cl^-. \qquad (XVIII)$$

Hence one has the equilibrium condition

$$c_{Pb^{2+}\bullet} \times c_{\square} = L_{PbCl_2} \qquad (XIX)$$

where the concentration of Cl^- ions on normal lattice sites is omitted because this concentration is constant.

From equation (XIX) it follows that another solute which increases the concentration of cation vacancies will decrease the equilibrium concentration of lead in AgCl as solvent in equilibrium with solid lead chloride. This has been confirmed experimentally with $CdCl_2$ as second solute by Wagner and Zimens (46). Results for small additions of $CdCl_2$ (up to about 0.8 molar per cent) agree with values predicted by using the ideal law of mass action, but deviations occur at higher concentrations of $CdCl_2$ in the same manner as in aqueous solutions because of electrostatic ionic interaction (47).

The Mechanism of Electronic Conduction

In a pure ionic crystal with an ideal stoichiometric ratio of metal to nonmetal, electronic conduction becomes possible by a disorder equilibrium of electrons which is analogous to the Frenkel disorder equilibrium for cations. The first theoretical treatment has been given by Wilson (48).

At low temperatures, practically all electrons are bound in the shells of the constituent ions of the crystal. At higher temperatures, however, some electrons assume a higher energy characteristic of the "conduction band," thus leave their low energy positions, migrate at random as "interstitial electrons," "quasi-free electrons," or "excess electrons," and contribute to electronic conduction. In addition, there is the possibility of an exchange of electrons between ions with normal shells and ions with incomplete shells, having an "electron vacancy" or an "electron hole."

As an analogue to equation (IV) one has

$$e^- = \ominus + \oplus \qquad (XX)$$

where e^- denotes an electron bound in the lattice, $\ominus$ an excess electron, and $\oplus$ an electron hole, representing an excess positive charge in comparison to an ideal lattice region.

Since the electron shells of the ions of a lattice overlap, electrons cannot be assigned unambiguously to a particular constituent of the lattice. In view of the behavior of gaseous or dissolved ions with different valence states, however, one may interpret excess electrons and electron holes in terms of ions having an anomalous valence state. For instance, an excess electron in CuO may be interpreted as an electron associated with a Cu^{++} ion, i.e., a Cu^+ ion, whereas an electron hole in CuO may be formulated as a Cu^{3+} ion, which has one electron less than the ubiquitous Cu^{++} ions (49). In view of the overlapping electron shells these formulations represent only a first approximation, from which closer approximations may eventually be obtained as has been shown by Dressnandt (50).

In the "chemical theory" used preferably in this review, the location of the electron is the primary factor, whereas in the "band theory" based on concepts of wave mechanics the energy of the electron is the primary factor. Both factors are, of course, interrelated. Chemical theory and band theory are approximations and supplement each other as has been pointed out by Wagner (49, 51), Schottky (52), Stöckmann (53), and others.

In a pure ionic compound having the ideal stoichiometric composition, the concentration of excess electrons and electron holes must be equal,

$$c_{\ominus} = c_{\oplus}. \qquad (XXI)$$

This is the condition for so-called intrinsic semiconductors, which is an analogue to equation (VI) for ionic conductors.

Under most conditions, however, equation (XXI) does not

apply because of small deviations from the ideal stoichiometric ratio of metal to nonmetal as has been pointed out by Gudden (54), Wagner (55), Meyer (56), and others. Since in most cases the significant deviations from the ideal stoichiometric ratio of metal to nonmetal are extremely small, it is profitable to replace this ratio by the nonmetal partial pressure in a coexisting gas atmosphere as an independent thermodynamic variable. At high temperatures, the electronic conductivity of many oxides, sulfides, and halides has been found to be a single-valued function of the partial pressure of nonmetal over the sample (10, 16, 55, 57–68). For instance, in the case of ZnO, the electrical conductivity at 600°C is approximately inversely proportional to the fourth root of the oxygen partial pressure. By and large, an increase of the conductivity with decreasing nonmetal partial pressure (increasing metal partial pressure) indicates that conduction is mainly due to an excess of metal, presumably present in the form of metal ions and quasi-free electrons (n-type semiconductor). The excess metal ions may occupy interstitial lattice sites as is probable in the case of zinc oxide (57). In contrast, TiO with excess titanium contains anion vacancies rather than interstitial cations (69).

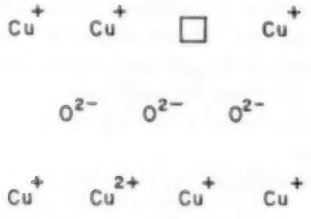

FIG. 6. Lattice defects in Cu_2O with oxygen excess (= metal deficit).

The electrical conductivity of cuprous oxide at 1000°C is proportional to the seventh root of the oxygen partial pressure (10). An increase of the electrical conductivity with increasing nonmetal partial pressure (decreasing metal partial pressure) indicates that electronic conduction is mainly due to an excess of nonmetal, equivalent to a deficit of metal. In this case, the electrical conductivity is mainly determined by electron holes (p-type semiconductor). A model of cuprous oxide is shown schematically in Fig. 6, where cation vacancies are indicated by a square, and electron holes are formulated as Cu^{2+} ions, i.e., copper ions which have one electron less than the surrounding monovalent copper ions. The oxygen take-up of cuprous oxide may be expressed by the stoichiometric equation

$$O_2(\text{gas}) + 4\,Cu^+ + 4\,e^- = Cu_2O + 4 \text{ cation vacancies} + 4\oplus. \quad \text{(XXII)}$$

Thus the ideal law of mass action gives the equilibrium condition

$$\frac{c_\square^4 \times c_\oplus^4}{p_{O_2}} = K \quad \text{(XXIII)}$$

where $c_\square$ is the concentration of cation vacancies.

If there are no other disorder equilibria, it follows from equation (XXII) that

$$c_\square = c_\oplus. \quad \text{(XXIV)}$$

Upon combining equations (XXIII) and (XXIV),

$$c_\square = c_\oplus = (K p_{O_2})^{\frac{1}{8}}. \quad \text{(XXV)}$$

Hence, if the mobility of electron holes is independent of concentration, the electrical conductivity due to electron holes becomes proportional to the eighth root of the oxygen partial pressure in close agreement with the experimental result mentioned above.

A similar situation is found in FeO, CoO, and NiO. For a given temperature and ambient oxygen partial pressure, the concentrations of cation vacancies and electron holes are much higher in FeO than in CoO, and those in CoO are higher than those in NiO (57, 59) in accordance with the relative stability of the trivalent state of Fe, Co, and Ni in aqueous solutions and under other conditions. This illustrates the heuristic value of the chemical interpretation of electron holes.

By and large, p-type conduction is favored if the cations of a compound tend to assume a higher valence state, whereas n-type conduction is favored if the cations tend to assume a lower valence state (55).

Some compounds exhibit both p-type and n-type conduction, depending on the chemical conditions (70). For instance, the electrical conductivity of PbS decreases with increasing sulfur partial pressure if the sulfur partial pressure is low and, accordingly, an excess of metal is present. On the other hand, the electrical conductivity increases with increasing sulfur partial pressure if the sulfur partial pressure is high and there is an excess of sulfur or deficit of metal. At an intermediate sulfur partial pressure, PbS assumes the ideal stoichiometric composition with equal concentrations of excess electrons and electron holes. Thus, a given compound may be an intrinsic semiconductor ($c_\ominus \cong c_\oplus$), an n-type semiconductor ($c_\ominus \ll c_\oplus$), or a p-type semiconductor ($c_\oplus \gg c_\ominus$) under different chemical conditions.

A similar behavior is found in the case of the chemical elements Si and Ge, which also may be intrinsic, n-type, or p-type semiconductors, depending on temperature and the content of foreign elements such as P and B, which are either electron donors or electron acceptors (71–72).

The systems mentioned thus far show a relatively simple behavior. In addition, there are more complex cases involving more than two types of lattice defects. A general theory of such equilibria has been presented by Schottky (52).

Pohl, Hilsch, Mollwo, and their associates have thoroughly investigated the behavior of alkali halides under various conditions (73, 74). In alkali halides with excess of alkali metal, most of the electrons are trapped in anion vacancies (F centers). The electronic component of the conductivity is determined by the temperature dependent equilibrium between trapped and free electrons because only free electrons contribute to the electrical conductivity. In addition to F centers, there are other centers each of which is characterized by a particular absorption band.

Association equilibria between lattice defects of opposite sign of the effective electrical charge will become particularly important at lower temperatures. The large variability of the electrical conductivity of Cu_2O at room temperature, ranging from 10^{-2} to 10^{-10} ohm^{-1} cm^{-1} (75) and the great influence of the cooling rate of the samples suggests that the formation of clusters as prestages for the precipitation of other phases such as CuO may also play an important part. At the present the behavior of such systems, which seemingly are not in a state of complete thermodynamic equilibrium, is not well understood.

New interesting features are found in ternary systems, especially at higher temperatures at which the aforementioned complications may be disregarded. Verwey (76), Wagner (77), Hauffe (78–83), and their associates have shown

that the electrical conductivity of oxides and sulfides under a given nonmetal partial pressure may be changed considerably by small amounts of other ionic compounds which increase or decrease the concentration of interstitial ions or vacancies and thereby increase or decrease the excess or the deficit of metal, i.e., the concentration of excess electrons or electron holes.

For instance, the electrical conductivity of ZnO at 600°C under an oxygen partial pressure of 1 atm is increased by a factor of 50 upon addition of 1 weight per cent Ga_2O_3 (77). Since Ga_2O_3 contains only $\frac{2}{3}$ cation for each anion, there will be cation vacancies in a solid solution of Ga_2O_3 in ZnO without excess of metal. Cation vacancies favor the take-up of excess zinc in form of zinc ions and excess electrons. Thus the electrical conductivity of a solid solution ZnO + Ga_2O_3 is higher than that of ZnO under a given oxygen partial pressure. Similar effects have been obtained with Al_2O_3 and Cr_2O_3 as solutes, whereas Li_2O having an excess of cations has the opposite effect (79).

In nickel oxide the situation is reverse. The electrical conductivity of NiO is increased by addition of Li_2O (76, 80). A solid solution of Li_2O in NiO without excess or deficit of metal may be formed with one anion vacancy for each Li_2O present. Thus the take-up of oxygen will be favored. Each oxygen atom entering the lattice needs two electrons in order to form an oxygen ion and thus creates two electron holes, i.e., Ni^{3+} ions. As a limiting case, one may expect that each Li_2O leads to the formation of 2 Ni^{3+} ions. This scheme has been confirmed by the observation that the electrical conductivity of a solid solution NiO + Li_2O at 1000°C is proportional to the Li_2O content and independent of the ambient oxygen partial pressure (80). In contrast, the electrical conductivity of NiO without Li_2O is about proportional to the fourth root of the oxygen partial pressure as has been mentioned above.

Dissolution of Cr_2O_3 in NiO leads to the formation of cation vacancies. Thus the formation of additional cation vacancies resulting from the take-up of oxygen becomes less probable and the electrical conductivity of a solid solution NiO + Cr_2O_3 is considerably less than that of NiO under a given oxygen partial pressure (80).

Diffusion Process and Chemical Reactions Involving Ionic Crystals

In reactions involving solids, the reactants frequently become separated from each other by a coherent layer of the reaction product. Then the reaction can proceed only as far as the reactants diffuse across the separating layer. In ionic crystals it is plausible to assume that the elementary diffusing particles are ions and electrons. In many cases, the migration of electrically neutral particles seems negligible, although in some cases electrically neutral particles do migrate, e.g., I_2 molecules in KI, presumably via cation-anion pair vacancies, as has been shown by Mollwo (84). By and large, the electrochemistry of ionic crystals is closely interrelated to the kinetics of chemical reactions involving ionic crystals as reaction products. In particular, if the reaction is diffusion controlled, and electrically neutral particles do not migrate appreciably, it is possible to calculate the rate from electrochemical measurements on the reaction product (85–91). Moreover, one may predict whether additives will increase or decrease the concentration of mobile ions and electrons by changing the concentration of interstitial particles or vacancies, and accordingly will increase or decrease reaction rates (92–97).

The following types of reactions have been investigated.

1. If a metal is exposed to air at elevated temperatures, an oxide layer is formed on the surface of the metal. In many cases the rate is inversely proportional to the instantaneous thickness of the oxide layer, and accordingly the thickness increases proportionally to the square root of time (parabolic rate law) as has been found first by Tammann (98) and Pilling and Bedworth (99). This indicates that the reaction is essentially diffusion controlled. If copper is oxidized in air of atmospheric pressure at 1050°C, only cuprous oxide, Cu_2O, is formed. From electrochemical investigations it is known that copper ions can migrate via cation vacancies, and electrons via electron holes. Thus, according to Wagner (85), the formation of cuprous oxide may be interpreted by migration of copper ions and electrons from the Cu/Cu_2O interface to the outer Cu_2O surface where oxygen is available and new lattice layers of cuprous oxide are formed. This working hypothesis leads to a formula for the calculation of the oxidation rate from the electrical conductivity of cuprous oxide and the transference number of copper ions as functions of the oxygen partial pressure of a coexisting gas atmosphere. The validity of this formula has been confirmed by Wagner and Grünewald (87).

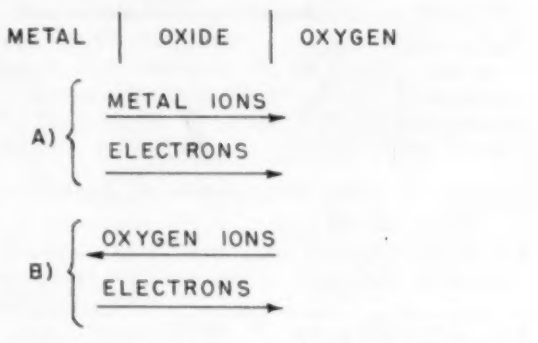

FIG. 7. Migration processes in an oxide layer during the oxidation of a metal.

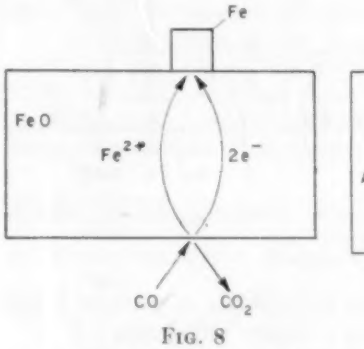

FIG. 8

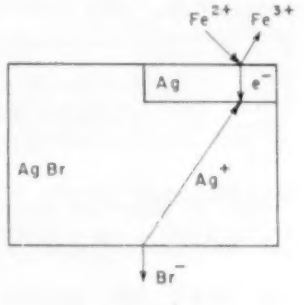

FIG. 9

FIG. 8. Reduction of iron oxide by means of CO

FIG. 9. Reduction of AgBr by ferrous salt in aqueous solution.

Wagner's general scheme is shown in Fig. 7. In many cases, cations rather than anions migrate. In magnetite, however, the migration of anions also contributes to the observed oxidation rate as has been shown by Davies, Simnad, and Birchenall (100). In other cases, preponderating anion migration is probable (88), although there is not yet a direct experimental proof.

2. Migration of ions and electrons also plays an important part in the reduction of oxides, sulfides, and halides (101–103), e.g., in the reduction of iron oxide by means of CO as is shown in Fig. 8. Mott and Gurney (104, 105) and others (106, 107) have suggested a similar mechanism for the development of the latent image of the photographic plate (Fig. 9). This mechanism is supported by recent experiments carried out by

Jaenicke, Krüger, and Hauffe (108). According to these authors the rate of the reduction of AgBr on a silver foil by means of ferrous oxalate in aqueous solution is considerably increased by connecting the silver foil covered by AgBr with another bright silver foil which is more accessible to ferrous oxalate.

In addition to the mechanisms shown in Fig. 8 and 9, however, there are direct reactions at the three-phase boundaries metal/compound/gas or liquid containing the reducing agent (109, 110).

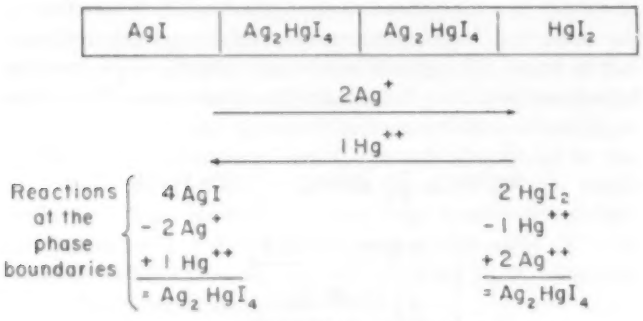

FIG. 10. Formation of Ag_2HgI_4

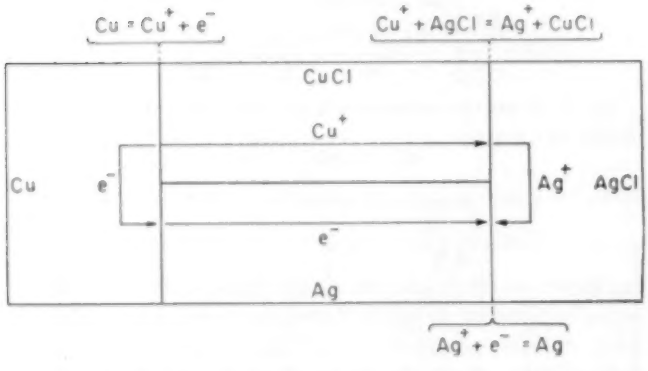

FIG. 11. Migration processes accounting for the reaction Cu + AgCl = Ag + CuCl.

3. Simple ionic compounds frequently combine with each other and form compounds of higher order, e.g.,

$$2\,AgI + HgI_2 = Ag_2HgI_4. \qquad \text{(XXVI)}$$

The reaction product separates the reactants from each other. It seems plausible to assume migration of ions rather than migration of molecules. According to Koch and Wagner (90) Ag^+ and Hg^{++} ions migrate in opposite directions (Fig. 10). The mechanism of the formation of spinells and silicates has not yet been clarified (111).

4. According to Wagner (91), migration of ions (and electrons) also makes possible reactions with two solid reaction products, e.g., AgCl + Cu = CuCl + Ag, 2 AgCl + Pb = $PbCl_2$ + 2 Ag, Co + Cu_2O = CoO + 2 Cu, AgCl + NaI = AgI + NaCl (Fig. 11).

In the aforementioned reactions there must be gradients of the chemical potentials of the components, or gradients of composition corresponding to the different boundary conditions at the interfaces with the different reactants (e.g., Cu/Cu_2O and Cu_2O/O_2). Consequently, a thorough knowledge of the electrochemistry of the ionic crystals involved is necessary before a detailed theoretical analysis of diffusion processes determining the rate of a chemical reaction can be made (86–88).

Conclusions

In spite of some analogies, the electrochemistry of ionic crystals is more complex than the electrochemistry of aqueous solutions. Even in the case of a pure compound, there are, in principle, six types of lattice defects which may contribute to the electrical conductivity, viz., (*a*) interstitial cations, (*b*) cation vacancies, (*c*) interstitial anions, (*d*) anion vacancies, (*e*) excess electrons, and (*f*) electron holes. In general, some types of lattice defects will be negligible. But much skill and labor are needed in order to ascertain the validity of simplifying assumptions. In addition to the aforementioned lattice defects, there may be electrically neutral defects such as cation-anion pair vacancies, electrons associated with an anion vacancy (F centers), and other "associated" complexes. Thus the variety of lattice defects is similar to the variety of constituents in an aqueous solution of CdI_2 or $HgCl_2$.

In addition to investigations on pure compounds, investigations on solid solutions involving known or thermodynamically defined concentrations of solutes are particularly important. In many cases, the electrical conductivity of a substance having an excess of metal or nonmetal, or containing a foreign ionic compound is much greater than the electrical conductivity of the pure solvent. Then, for most purposes, one may disregard defects prevailing in the pure substance for the same reason as one may disregard the dissociation of water in many investigations with aqueous solutions. The presence of a well-defined excess of metal or nonmetal and of definite amounts of foreign substances has particular importance for the industrial production of semiconductors with reproducible qualities.

To illustrate the leading principles, typical and seemingly simple systems have been quoted. The existence of more complex situations, however, must not be overlooked.

It is shown how the constitution of the various systems can be derived from the results of conductivity and transference measurements, equilibrium investigations, and x-ray investigations. The conclusions are supported by the results of other methods, e.g., measurements of the Hall effect, the thermoelectric power, optical properties, etc., which are not discussed in this review.

It is also shown how the results of electrochemical investigations on ionic crystals may be applied to the interpretation of the kinetics of chemical reactions involving diffusion processes in ionic crystals. The interpretation of catalytic reactions on the surface of ionic crystals is another important application (112–119) but is beyond the scope of this review.

REFERENCES

1. E. WARBURG, *Wiedem. Ann. Physik*, **21**, 622 (1884); E. WARBURG AND F. TEGETMEIER, *Wiedem. Ann. Physik*, **32**, 442 (1887); **35**, 455 (1888); F. TEGETMEIER, *Wiedem. Ann. Physik*, **41**, 18 (1890).
2. F. HABER AND A. TOLLOCZKO, *Z. anorg. Chem.*, **41**, 407 (1904).
3. E. BRUNI AND O. SCARPA, *Rend. reale accad. naz. Lincei*, **22**, 438 (1913).
4. C. TUBANDT AND F. LORENZ, *Z. physik. Chem.*, **87**, 513 (1914).
5. C. TUBANDT AND S. EGGERT, *Z. anorg. u. allgem. Chem.*, **110**, 196 (1920).
6. C. TUBANDT, "Handbuch der Experimentalphysik," edited by W. Wien and F. Harms, Vol. 12, Part 1, p. 383, Akademische Verlagsgesellschaft, Leipzig (1932).
7. C. TUBANDT, *Z. anorg. u. allgem. Chem.*, **115**, 105 (1921).
8. C. TUBANDT AND H. REINHOLD, *Z. Elektrochem.*, **29**, 313 (1923).

9. C. Tubandt, H. Reinhold, and G. Liebold, *Z. anorg. u. allgem. Chem.*, **197**, 225 (1931).
10. H. Dünwald and C. Wagner, *Z. physik. Chem. B*, **22**, 212 (1933).
11. J. Gundermann and C. Wagner, *Z. physik. Chem. B*, **37**, 155 (1937).
12. C. Wagner, *Z. physik. Chem. B*, **21**, 42 (1933); **23**, 469 (1934).
13. C. Tubandt and H. Reinhold, *Z. physik. Chem. B*, **24**, 22 (1934)
14. C. Tubandt, E. Rindtorff, and W. Jost, *Z. anorg. u. allgem. Chem.*, **165**, 195 (1927).
15. J. N. Frers, *Ber.*, **57**, 1693 (1924); **60**, 864 (1927); J. N. Frers and F. Leopold, *Ber.*, **61**, 377 (1928).
16. K. Nagel and C. Wagner, *Z. physik. Chem. B*, **25**, 71 (1934).
17. J. Frenkel, *Z. Physik*, **35**, 652 (1926).
18. L. W. Strock, *Z. physik. Chem. B*, **25**, 441 (1934); **31**, 132 (1935).
19. P. Rahlfs, *Z. physik. Chem. B*, **31**, 157 (1935).
20. J. A. A. Ketelaar, *Z. Krist.*, **87**, 436 (1934).
21. W. Schottky, *Z. physik. Chem. B*, **29**, 335 (1935).
22. W. Jost and G. Nehlep, *Z. physik. Chem. B*, **32**, 1 (1936).
23. N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.*, **34**, 485 (1938).
24. E. S. Rittner, R. A. Hutner, and K. F. du Pré, *J. Chem. Phys.*, **17**, 198, 204 (1949); **18**, 379 (1950).
25. E. Koch and C. Wagner, *Z. physik. Chem. B*, **38**, 295 (1937).
26. F. Kohlrausch and A. Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894).
27. J. Teltow, *Ann. Physik*, (6), **5**, 63, 71 (1950).
28. J. Teltow, *Z. physik. Chem.*, **195**, 213 (1950).
29. C. Wagner and J. Beyer, *Z. physik. Chem. B*, **32**, 113 (1936)
30. C. R. Berry, *Phys. Rev.*, **82**, 422 (1951).
31. W. Jost and G. Nehlep, *Z. physik. Chem.*, **34**, 348 (1936).
32. W. Jost and S. Mennenöh, *Z. physik. Chem.*, **196**, 188 (1950).
33. J. W. Mitchell, *Phil. Mag.*, (7), **40**, 249 (1949).
34. O. Stasiw, *Z. Physik*, **127**, 522 (1950).
35. H. Kelting and H. Witt, *Z. Physik*, **126**, 697 (1949).
36. C. Wagner and P. Hantelmann, *J. Chem. Phys.*, **18**, 72 (1950).
37. H. W. Etzel and R. J. Maurer, *J. Chem. Phys.*, **18**, 1003 (1950).
38. U. Haven, *Rec. trav. chim.*, **69**, 1259, 1471 (1950).
39. U. Croatto and M. Bruno, *Gazz. chim. ital.*, **78**, 95 (1948); C. Wagner, *Naturwissenschaften*, **31**, 265 (1943); F. Hund, *Z. Elektrochem.*, **55**, 363 (1951).
40. U. Croatto and A. Mayer, *Gazz. chim. ital.*, **73**, 199 (1943).
41. C. Fritsch, *Wiedemann Ann. Physik*, **60**, 300 (1897).
42. M. Le Blanc, *Z. Elektrochem.*, **18**, 549 (1912).
43. R. Ketzer, *Z. Elektrochem.*, **26**, 77 (1920).
44. C. Tubandt and H. Reinhold, *Z. Elektrochem.*, **29**, 313 (1923).
45. Z. Gyulai, *Z. Physik*, **67**, 812 (1931).
46. C. Wagner and K. E. Zimens, *Acta Chem. Scand.*, **1**, 539 (1947).
47. O. Schaerer, *Physik. Z.*, **25**, 145 (1924).
48. R. Wilson, *Proc. Roy. Soc. (London) A*, **133**, 458 (1931); **134**, 277 (1932).
49. H. H. von Baumbach, H. Dünwald, and C. Wagner, *Z. physik. Chem. B*, **22**, 226 (1933).
50. H. Dressnandt, *Z. Physik*, **115**, 369 (1940).
51. C. Wagner, *Physik. Z.*, **36**, 721 (1935).
52. W. Schottky, *Z. Elektrochem.*, **45**, 33 (1939).
53. F. Stöckmann, *Z. physik. Chem.*, **198**, 215 (1951).
54. B. Gudden, *Ber. Physik. Medizn. Soz. Erlangen*, **62**, 289 (1930); *Ergeb. exakt. Naturw.*, **13**, 223 (1934).
55. C. Wagner, *Z. physik. Chem. B*, **22**, 181 (1933).
56. W. Meyer, *Z. Physik*, **85**, 278 (1933).
57. H. H. von Baumbach and C. Wagner, *Z. physik. Chem. B*, **22**, 199 (1933).
58. H. H. von Baumbach and C. Wagner, *Z. physik. Chem. B*, **24**, 59 (1934).
59. C. Wagner and E. Koch, *Z. physik. Chem. B*, **32**, 439 (1936).
60. H. Reinhold and K. Schmitt, *Z. physik. Chem. B*, **44**, 75 (1939).
61. K. Hauffe, *Z. physik. Chem. B*, **48**, 124 (1941).
62. R. J. Maurer, *J. Chem. Phys.*, **13**, 321 (1945).
63. B. H. Vine and R. J. Maurer, *Z. physik. Chem.*, **198**, 147 (1951).
64. C. A. Hogarth, *Phil. Mag.*, (7) **39**, 260 (1948).
65. C. A. Hogarth, *Z. physik. Chem.*, **198**, 30 (1951).
66. R. Mansfield, *Proc. Phys. Soc. B*, **62**, 476 (1949).
67. P. H. Miller, *Phys. Rev.*, (2) **60**, 890 (1941).
68. R. W. Wright and J. R. Andrews, *Proc. Phys. Soc. (London) A*, **62**, 446 (1949).
69. P. Ehrlich, *Z. Elektrochem.*, **45**, 362 (1939).
70. K. Bauer, *Ann. Physik*, (5) **38**, 84 (1940); L. Eisenmann, *Ann. Physik*, (5) **38**, 121 (1940); H. Hintenberger, *Z. Physik*, **119**, 1 (1942); M. C. Morton, *Trans. Faraday Soc.*, **43**, 194 (1947).
71. K. Lark-Horovitz, A. E. Middleton, E. P. Miller, and J. Wallerstein, *Phys. Rev.*, **69**, 258 (1946).
72. G. L. Pearson and W. Shockley, *Phys. Rev.*, (2) **71**, 142 (1947); G. L. Pearson and W. Bardeen, *Phys. Rev.*, **75**, 865 (1949).
73. R. W. Pohl, *Physik. Z.*, **39**, 36 (1938); *Proc. Phys. Soc. (London)*, **49**, (Extra part), 3 (1937).
74. F. Seitz, *Revs. Mod. Phys.*, **18**, 384 (1946).
75. F. Waibel, *Z. tech. Physik*, **16**, 366 (1935).
76. E. J. W. Verwey, P. W. Haayman, and F. C. Romeyn, *Chem. Weekblad*, **44**, 705 (1948); E. J. W. Verwey, *Bull. soc. chim. France*, **1949**, D 93.
77. C. Wagner, *J. Chem. Phys.*, **18**, 62 (1950).
78. K. Hauffe, *Ann. Physik*, (6) **8**, 201 (1950).
79. K. Hauffe and A. L. Vierk, *Z. physik. Chem.*, **196**, 160 (1950).
80. K. Hauffe and J. Block, *Z. physik. Chem.*, **196**, 438 (1950)
81. K. Hauffe and J. Block, *Z. physik. Chem.*, **198**, 232 (1951).
82. K. Hauffe and H. Grunewald, *Z. physik. Chem.*, **198**, 248 (1951)
83. K. Hauffe, *Ergeb. exakt. Naturw.*, **25**, 193 (1951).
84. E. Mollwo, *Ann. Physik*, (5) **29**, 394 (1937).
85. C. Wagner, *Z. physik. Chem. B*, **21**, 25 (1933).
86. C. Wagner, *Z. physik. Chem. B*, **32**, 447 (1936).
87. C. Wagner and K. Grünewald, *Z. physik. Chem. B*, **40**, 455 (1938).
88. C. Wagner, "Diffusion and High Temperature Oxidation of Metals" in "Atom Movements," p. 153, American Society for Metals, Cleveland, Ohio (1950).
89. C. Wagner, *Z. physik. Chem. B*, **34**, 309 (1936).
90. E. Koch and C. Wagner, *Z. physik. Chem. B*, **34**, 317 (1936).
91. C. Wagner, *Z. anorg. allgem. Chem.*, **236**, 320 (1938).
92. C. Wagner and K. E. Zimens, *Acta Chem. Scand.*, **1**, 547 (1947).
93. W. Himmler, *Z. physik. Chem.*, **195**, 129 (1950).
94. K. Hauffe and C. Gensch, *Z. physik. Chem.*, **195**, 116 (1950).
95. C. Gensch and K. Hauffe, *Z. physik. Chem.*, **195**, 386 (1950).
96. C. Gensch and K. Hauffe, *Z. physik. Chem.*, **196**, 427 (1951).
97. K. Hauffe, *Werkstoffe u. Korrosion*, **1**, 131, 221, 243 (1951).

98. G. Tammann, *Z. anorg. allgem. Chem.*, **111**, 78 (1920).
99. N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923).
100. M. H. Davies, M. T. Simnad, and C. E. Birchenall, *Trans. AIME*, **191**, 889 (1951).
101. N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," p. 263. At the Clarendon Press, Oxford (1940).
102. O. H. Gellner and F. D. Richardson, *Nature*, **168**, 23 (1951).
103. C. Wagner, *Trans. AIME*, **194**, 214 (1952).
104. R. W. Gurney and N. F. Mott, *Proc. Roy. Soc. (London) A*, **164**, 151 (1938).
105. N. F. Mott, *J. phys. radium*, **7**, 249 (1946).
106. W. Berg, *Trans. Faraday Soc.*, **39**, 15 (1943).
107. Kh. S. Bagdasar'yan, *Acta Physicochim. U.R.S.S.*, **19**, 421 (1944); **20**, 441 (1945).
108. W. Jaenicke, A. Krüger, and K. Hauffe, *Z. physik. Chem.*, **197**, 161 (1951).
109. G. M. Schwab and E. Pietsch, *Z. Elektroche ..*, **35**, 5 (1929).
110. T. H. James, "Catalytic Phenomena Related to Photographic Development" in "Advances in Catalysis and Related Subjects," edited by W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Vol. 2, pp. 105 Academic Press, New York, (1950).
111. G. Cohn, *Chem. Revs.*, **42**, 527 (1948).
112. C. Wagner and K. Hauffe, *Z. Elektrochem.*, **44**, 172 (193
113. C. Wagner, *J. Chem. Phys.*, **18**, 69 (1950).
114. W. E. Garner, T. J. Gray, and F. S. Stone, *Proc. Roy. Soc. A*, **197**, 294 (1949); *Disc. Faraday Soc.*, **8**, 246 (1950)
115. W. E. Garner, *Proc. Roy. Soc. A (London)*, **197**, 3 (1949).
116. T. J. Gray, *Disc. Faraday Soc.*, **8**, 331 (1950).
117. J. S. Anderson, *Disc. Faraday Soc.*, **4**, 163 (1948).
118. D. A. Dowden, *J. Chem. Soc.*, **1950**, 242.
119. D. J. M. Bevan and J. S. Anderson, *Disc. Faraday Soc.* **8**, 238 (1950).

ELECTROCHEMISTRY IN BIOLOGY (1902—52)

L. G. Longsworth[1]

In opening a recent conference on bioelectric phenomena, W. J. V. Osterhout (1) invoked the ghost of Luigi Galvani to engage in the following conversation with the conference participants:

"In 1791 I published some observations on frogs legs. I noticed that in contact with copper and iron they twitched vigorously. Can you tell me why this happens?"

"We fear that we cannot give you a satisfactory answer. In spite of much study the cause is not clear."

"It is a long time," he answers, "since the first observations were made."

Yes, it has been a long time but the problems posed by this experiment are fundamental ones indeed. Included are the bio- and mechanochemistry of muscular activity, the nature and conductance mechanism of the nerve impulse and, of most interest to the electrochemist, the phenomena accompanying the transport of charged particles in solution and across phase boundaries.

Actually, much has been learned about ionic transport in solution, otherwise known as electrophoresis. Almost entirely within the lifetime of The Electrochemical Society, it has been developed into a tool of particular value to biochemical and medical research. Consequently, it will be one of the topics considered in this survey.

It was also recognized quite early that when two conducting, homogenous phases were placed in contact a difference of electric potential between them could be expected. Different names have been assigned to the various possibilities. Those of most interest to us are the contact potential between two metals, the electrode potential between a metal and a conducting solution, the liquid junction potential between two solutions in a common solvent, and the phase boundary potential between two immiscible solutions. In any complete electric circuit designed to measure these potentials at least three of them must be present and the combination is quite fittingly known as a galvanic cell. All of the possibilities mentioned above doubtless contributed to Galvani's original observation.

Within the lifetime of this Society the galvanic cell has been used in innumerable researches of interest to the biologist. These include studies of acid-base and oxidation-reduction equilibria and the development and application of the polarograph. Metals are, however, not constituents of living matter. Thus, in physiology, it is the electrochemists' work on liquid junction and phase boundary potentials that has found application, and this will receive special attention in a brief review of galvanic cell development

Electrophoresis

It was soon after the turn of the century that Hardy (2) first included the moving boundary method as one of several techniques in a remarkable investigation of serum globulin. After dialysis of a solution of this material against dilute acetic acid he formed a boundary between the solution and the dialysate in each side of a U-tube by allowing the heavier protein solution to flow under the acetic acid from a reservoir connecting with the bottom of the U. On application of a potential difference between electrodes dipping into the acetic acid above the boundaries, he observed that the one boundary, rendered visible by the opalescence of the protein solution, rose toward the cathode, while that in the other side of the tube descended. If the globulin was dissolved in dilute alkali the boundaries moved anodically, thus confirming the amphoteric nature of the protein.

Solutions of many proteins are, however, quite clear and the boundaries correspondingly difficult to see. Many subsequent workers resorted, therefore, to the Hittorf, or transference method as it is sometimes called, to determine the mobilities of protein ions. Much of this work had as its chief object the determination of the *p*H at which the protein does not move in an electric field, i.e., its isoelectric *p*H. This was true of the work of Michaelis and his associates (3). To him we are indebted for emphasizing the necessity of controlling, with the aid of buffers, the *p*H of the protein solution and for introducing the use of reversible, nongassing electrodes.

The outstanding developments in the electrophoresis of proteins by the moving boundary method were made, however, by Tiselius (4). In 1937 he described "A New Apparatus for Electrophoretic Analysis of Colloidal Mixtures" that has developed into one of the most useful tools of biology and medicine. In order to increase the precision of the method as applied to proteins, Tiselius designed a cell in which the initially sharp boundaries between protein and buffer solutions, that are essential to the success of an experiment, are formed by a shearing technique, as in a stopcock, and with which the Foucault-Toepler schlieren optical method could be used to observe and photograph the changes of refractive index that inevitably occur at such boundaries. Also essential to the best performance of this equipment is the use of a thermostat regulating near the temperature of maximum density of the solution, i.e., $t \leq 4°$. Advantage is thereby taken of the fact that in such a thermostat the temperature gradients developed in dissipating the heat produced by the current are not accompanied by significant differences of density. At other temperatures the boundaries are frequently disturbed or destroyed by the convection resulting from these density gradients.

Although the Tiselius method is widely used to determine the mobilities of protein ions, its most important application has been for the analysis of mixtures such as blood serum (5–8). This application is possible because the mobilities of the various proteins that may be present in a mixture usually differ from each other. Initially, each species occupies the same portion of the channel but on passage of the current the zone in which a given protein is present moves at a rate proportional to its mobility and thus progressively separates from zones occupied by species having different mobilities. Thus, in the ideal case the initial boundary in each side of the channel splits, on passage of the current, into a number of separated boundaries equal to the number of species having different mobilities. Below each of these separated boundaries a species is present at the same concentration as in the original mixture but absent above and is said to disappear across the boundary. Owing to the close proportionality between refractive index and concentration, measurement of the difference in this index across each boundary affords an analysis of the mixture.

In recent years the methods for the measurement of the

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refractive indexes in, and across, the boundaries have been extended and improved so that a precision of 2×10^{-7} in this index is now attainable (5). Owing, however, to uncertainties in the interpretation of the boundary patterns the precision in the analyses has not kept pace. The difficulty arises in the assumption of the ideality of the process, i.e., that the protein ions contribute to the refractive index of the solution but not to its conductance. At protein concentrations of a few per cent or less, and at *p*H values not too far removed from the isoelectric *p*H, the conductance due to the protein is small in comparison with that due to the buffer ions but is by no means negligible. Consequently, at each boundary across which a protein disappears there are superimposed small gradients of other species that render the refractive index difference for this boundary an approximate measure only of the concentration of the disappearing protein. While this is not a serious limitation of the method for comparative analyses, e.g., the blood serum proteins in health and disease, it is exasperating that the inherent precision of the method cannot be fully realized.

Undoubtedly, the most significant advance in moving boundary theory during the past half century has been the solution, by Dole (9), of the equations of ion transport for the general case of n species. If all n species are present in each of the two solutions forming the original boundary, the problem involves the solving of two polynomials, of degree $n - 2$, in the equivalent concentrations and mobilities of the n species. Although predicting qualitatively the electrophoretic behavior of real protein mixtures, this theory has two shortcomings. In common with most moving boundary theory, it is designed for the ions of strong electrolytes, i.e., those whose mobilities are essentially independent of *p*H. Solution of the protein in a buffer assures a relatively constant mobility only in so far as the *p*H does not change across a boundary but small changes do occur. Moreover, the Dole polynomials are difficult to cast into a form in which the observable quantities, i.e., boundary displacement and refractive index difference, can be utilized. Several laboratories are currently engaged in an effort to overcome these limitations of the Tiselius method.

Another limitation of the Tiselius method is the difficulty encountered in adapting it for preparative purposes on a large scale or for analysis on a micro scale. Moreover, in the unpacked channel of the Tiselius cell, gravitational stability requires that at each boundary the solution below be more dense than the one above. Since no boundary can move through the bottom of the U without violating this requirement, complete separation of the components of a mixture is not possible, the procedure being similar in this respect to frontal analysis in chromotography. If, however, the channel is packed with a stationary disperse phase (10), e.g., paper, agar, sand, starch, etc., separations resulting from ion migration can then occur in the capillary spaces of the packing without regard to gravitational stability. Thus, complete separations are sometimes possible as in the so-called elution analysis of chromotography. With the aid of sensitive color reagents to locate the "band" on the packing due to a given protein, or amino acid, qualitative analyses of mixtures of these materials are possible on a truly micro scale. Quantitative interpretation of the results is frequently complicated, however, by electroosmosis, by uncertainty as to the effective strength of the electric field, and by irreversible adsorption of the protein on the packing material. Electrophoresis in packed channels also lends itself readily to fairly large-scale preparative work.

Also useful as a preparative procedure is the electrophoresis-convection method of Kirkwood and his associates (11). Here the protein mixture is present in an upper and lower reservoir connected by a channel of rectangular cross-section one dimension of which is small, say 1 to 2 mm, while the other may be several cm or more. The separation of the reservoirs, i.e., the height of the channel, may be several times the long side of the rectangle. Since the walls of this channel must be permeable to salt and buffer ions, but impermeable to proteins, it is frequently made of dialysis tubing. The operation is simplest to understand if the channel is immersed in a buffer of a *p*H isoelectric with one of the proteins in the mixture. On passage of a current horizontally across the small dimension of the channel, the mobile protein components migrate to one wall where the resulting increase in density initiates and maintains a convective circulation between the two reservoirs that concentrates the mobile constituents in the bottom one and leaves a partially purified solution of the isoelectric protein in the top one.

Although the developments in electrophoresis discussed here have afforded the biochemist useful tools for the fractionation and characterization of the protein mixtures derived from living matter, it must be conceded that only indirectly have the results obtained advanced our understanding of the problems raised by Galvani's experiment. In the following discussion of galvanic cells it will become clear that very little is known regarding the nature and properties of the current carriers in the complex media of the cell membrane.

Galvanic Cells in Biology

Possibly the most important development in electrochemistry during the past fifty years has been the appreciation, largely through the work of G. N. Lewis, of the value of the galvanic cell without a liquid junction. With one exception to be noted below, only cells of this type yield results of significance for the thermodynamics of solutions of electrolytes. However, the galvanic cells used by the biologist, whether for the measurement of *p*H or in the study of cell membranes, almost invariably contain one or more liquid junctions. Moreover, the junctions encountered in work with living material are frequently of a type about which the electrochemist knows very little. Before considering these, however, it is of interest to review briefly what he has learned.

While the Arrhenius theory undoubtedly brought a welcome clarification into the electrochemistry of solutions, the faith in the reality of ions that it engendered also contributed to a conviction that the potential difference across a liquid junction was a measureable quantity. If one identifies, as did Planck and Henderson, the ion concentration, C_i, with the product of the stoichiometric concentration of the (uni-univalent) salt and the conductance ratio Λ_e/Λ_o, all terms in the expression for the liquid junction potential

$$E_L = \frac{RT}{\mathbf{F}} \int_I^{II} \sum_i t_i \, d \ln C_i \qquad (I)$$

are measureable and hence the potential itself. Here t_i is the Hittorf transference number and the integration for each species i is from the body of solution I to that of solution II. The fact that any complete circuit involving such a junction also includes at least two electrode potentials introduced no difficulty since Nernst's theory of these used the same ion concentrations.

An essential step in our disillusionment came when Lewis brought order out of chaos by introducing the concept of activity and showed that, for any reversible process, the

value of this property of a solute was independent of the method used for its measurement. If, however, an irreversible process, e.g., conductance in the case of strong electrolytes, was used, the ion concentration deduced therefrom differed from the activity. This discrepancy, together with the failure of the Arrhenius theory to describe the concentration dependence of the conductance, say, of these materials, came to be known as the "anomaly of strong electrolytes." Many investigators were convinced that these electrolytes were completely dissociated in aqueous solution even before the Debye-Hückel-Onsager theory confirmed this conviction by accounting for the concentration dependence, in dilute solutions at least, of both the activity and the conductance in terms of electrostatic interactions between the ions.

When written in terms of ion activities, a_i, the liquid junction equation

$$E_i = \frac{RT}{\mathbf{F}} \int_I^{II} \sum_i t_i \, d \ln a_i \qquad \text{(II)}$$

is more subtle. In practically all transport processes involving solutions of electrolytes, whether reversible or otherwise, electrical neutrality is preserved macroscopically and the materials whose transport is actually observed are electrically neutral substances. Although we can, and do, adopt the convention that the salt activity is the product of the activities of its ions Guggenheim (12) has reasoned convincingly that any attempt to assign numerical values to the ion activities will be arbitrary and not subject to experimental proof. It is now clear that the problem of individual ion activities and of the potential difference at a single junction or interface is really one and the same problem. Until a reversible transport process for a single charged species has been devised, we must be content with computations of ion activities and single potentials based upon assumptions that are reasonable but nevertheless inaccessible to experimental verification.

In many instances the measurements on a cell with a liquid junction are adequate in themselves. For example, the pH of a solution S given by the relation

$$p\mathrm{H} = \frac{E - 0.2466}{2.303\ RT/\mathbf{F}} \qquad \text{(III)}$$

where E is the emf of the cell

$$\mathrm{H_2};\ S\text{: KCl (satd.)};\ \mathrm{HgCl};\ \mathrm{Hg}$$

is a satisfactory measure of acidity for most applications in biology and medicine (13). It is only when one uses this pH to compute, with the aid of the relation

$$p\mathrm{H} = -\log C_{\mathrm{H}} f,$$

the hydrogen ion concentration, C_{H}, for comparison with values obtained by other methods that an assumption regarding the activity coefficient, f, must be made. Here the assumption is, and the constant in the numerator of equation (III) so selected, that f is the mean value, $f_{\pm}$, for the ions of acetic acid in dilute acetate buffers (14). Electrochemists are familiar with the importance of pH in biology and medicine, an importance that arises from the fundamental and all-pervading nature of the hydrated proton in the predominantly aqueous media of living tissue. Probably our most significant contribution to these sciences has been the development of tools, e.g., the hydrogen, glass, antimony, and quinhydrone electrodes, for use in the measurement of pH.

If practical to do so, cells with a liquid junction are, however, to be avoided. The early workers realized that E_L generally depended upon the distribution of ions in the junction and considerable effort was expended upon integration of equation (I) for various assumed distributions. Experimentally, this dependence results in the emf of the cell being a function of the manner in which the junction is formed and upon its "age." The exception noted above is the junction between two different concentrations of the same binary salt. Here the cell emf is quite independent of the distribution and, when combined with transference numbers, has provided some of our most precise thermodynamic data. Apparently the irreversible process of diffusion occurring at the junction in this cell does not invalidate it as a reversible electrochemical engine.

One of the clearest analyses of the cell with a liquid junction involving more than one binary salt is that of P. B. Taylor (15) who recognized the dual nature of the problem. Since the transference number of a given ion is a function of the concentration of all species that may be present the distribution of the ions in the junction must be known before equation (II) can be integrated. This is a problem in diffusion that has not been solved. Once the distribution and relevant transference numbers are known it is then possible to combine the processes occurring in the junction with those at the electrodes to obtain an exact expression for the cell emf involving measureable activities only.

In the case of plant cells, the physiologist is frequently interested in the comparatively steady potentials existing across their membranes and the manner in which these change with the environment. A typical problem is presented by the unicellular marine plant, Valonia macrophysa. Although essentially isotonic with sea water, the sap of this cell is 0.5 normal in potassium ion (16). Moreover, replacement of the sea water normally bathing the outer surface of this plant by sap, so that the internal and external fluids are identical, increases (17) the potential difference across the cell membrane from 10 to 65 mv instead of eliminating it completely as would be expected if the potential were due to simple ionic diffusion. Such a membrane is said to be asymmetric.

From the work of Michaelis (18), Osterhout (1), Teorell (19), Sievers (20), Sollner (21), and others, two alternative views have emerged as to the origin of this asymmetry. The one assumes the existence of nonaqueous films in which the concentrations and transference numbers of the ions are, presumably, quite different from their values in the aqueous phases. The other postulates a porous phase or sieve through the interstices of which the transport phenomena occur. The concentrations and transference numbers of the ions in the solution in the pores may differ from their values in the sap or external fluid as a result of the size of the pores and the presence of immobilized charges on the walls of the interstices.

Both approaches to the problem have, however, at least two features in common. In order to achieve asymmetry, it appears necessary to assume that the membrane is composite, i.e., it consists either of two nonaqueous films, separated by an intermediate aqueous layer (1), or of two porous phases, also separated by an aqueous layer (22). It is also customary to assume that the solutes are in equilibrium across the phase boundaries and that gradients of composition occur within the nonaqueous film on the one hand and the pores on the other. In either case, liquid junction theory is required but its application is handicapped by the meagerness of the data concerning the nature and properties of the carriers in liquids immiscible with water and in capillary spaces.

With the development of the ion exchange resins, thus giving the investigator a measure of control over both the

porosity and the nature and magnitude of the immobilized charge, the porous phase membrane is now being intensively studied (23). Membrane potentials are, however, only one aspect of the living cell and any valid concept of the membrane must be consistent with other properties as well. Thus, the permeability of cells to nonelectrolytes has long been considered as supporting the nonaqueous film concept (24).

In most of the experiments with the composite membranes described above, the emf arises from the free energy of dilution of the solution in the intermediate aqueous phase. In a recent development Shedlovsky (25) has described a "protochemical" cell in which the free energy of acid-base reactions, i.e., proton transfer, is made directly available as electrical work through the agency of protonic conductors. In one model of his composite membrane, the one face of a protonically-conducting glass film is reversible to hydrogen ions while to the other face is fused a mixture of insoluble lauric acid, HL, and its barium salt, thereby rendering this face reversible to the barium ion. With this composite membrane separating two portions of a buffered barium chloride solution an asymmetry potential is observed corresponding to the free energy of the reaction

$$\tfrac{1}{2}\,BaL_2 + HCl = HL + \tfrac{1}{2}\,BaCl_2.$$

Here the mobile protons in the glass function in a manner analogous to the electrons in a metal. The absence of metallic conductors in living matter, together with the fact that the energy is derived from a process other than the mere dilution of a solution, makes this development of especial interest to the physiologist.

Another common property of the living cell is its ability to maintain significant gradients of composition across its membrane in spite of the permeability of that membrane to the solutes concerned. Although numerous "pumping" mechanisms have been suggested, none has been shown to be operative in actual cells. The almost universal disappearance of the membrane potential on death suggests the cooperation of metabolic processes in its maintenance. Thus, the constancy with time reflects a steady state rather than an equilibrium and the Donnan effect, although frequently present, may not be as important a factor as was thought when it was introduced into biology by Loeb (26) a generation ago. In his search for coupling mechanisms between metabolic and electrochemical processes the biologist is turning to a rapidly developing field that is best described by the title of a recent monograph, "Thermodynamics of the Steady State" (27).

The problems encountered by the nerve physiologist are further complicated by the transient nature of many of the phenomena. Not only does the nerve cell have many of the properties already mentioned, but it also serves to conduct the impulse that controls muscular activity. Although the electrochemical effects accompanying the passage of the impulse have served as the principal means for the study of nervous activity, the true nature of the impulse is by no means completely understood. As in Galvani's experiment, this impulse is usually initiated, in the laboratory at least, electrically, and the investigator is thus concerned with the effects, on the membrane potential, of polarizing and depolarizing currents, both steady and alternating (28). A recent review, couched in terms familiar to electrochemists, is that of Hodgkin (29). Not only does he present the experimental results in an orderly fashion, but by vigorously espousing one of the prevalent theories in this controversial field the reader's interest is sustained.

In spite of its brevity and incompleteness, this survey will have served its purpose if it arouses the interest of electrochemists in some of the fascinating applications of their science to the problems of biology and medicine. To this end many of the references cited have been selected for the completeness and scope of their bibliographies.

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REFERENCES

1. W. J. V. Osterhout, *Proc. Nat. Acad. Sci.*, **35**, 548 (1949).
2. W. B. Hardy, *J. Physiol. (London)*, **33**, 251 (1905).
3. L. Michaelis, *et al.*, *Biochem. Z.*, **16**, 81, 486 (1909); **19**, 181 (1909); **24**, 79 (1910); **28**, 1, 193 (1910); **29**, 439 (1910); **33**, 456 (1911); **41**, 102, 373 (1912); **47**, 260 (1912); **67**, 198 (1914); **118**, 144 (1921).
4. Arne Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).
5. L. G. Longsworth, Vol. 5 "Methods in Medical Research," The Year Book Publishers, Inc., Chicago (1952).
6. J. A. Leutscher, Jr., *Physiol. Revs.*, **27**, 621 (1947).
7. K. G. Stern and Miriam Reiner, *Yale J. Biol. and Med.*, **19**, 67 (1946).
8. E. Wiedemann, *Experientia*, **3**, 341 (1947).
9. V. P. Dole, *J. Am. Chem. Soc.*, **67**, 1119 (1945).
10. H. G. Kunkel and Arne Tiselius, *J. Gen. Physiol.*, **35**, 89 (1951).
11. J. R. Cann, J. G. Kirkwood, R. A. Brown, and O. J. Plescia, *J. Am. Chem. Soc.*, **71**, 1603 (1949).
12. E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540, 1758 (1930).
13. Roger G. Bates, *Chem. Revs.*, **42**, 1 (1948).
14. D. A. MacInnes, "The Principles of Electrochemistry," p. 273, Reinhold Publishing Co., New York (1939).
15. P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).
16. W. J. V. Osterhout, *Ergeb. Physiol.*, **35**, 967 (1933).
17. L. R. Blinks, *Proc. Nat. Acad. Sci.*, **35**, 566 (1949).
18. L. Michaelis, *Bull. Nat. Research Council (U. S.) No. 69* (1929).
19. Torsten Teorell, *Proc. Soc. Exp. Biol. Med.*, **33**, 282 (1935).
20. K. H. Meyer and G. F. Sievers, *Helv. Chim. Acta*, **19**, 649 (1936).
21. Karl Sollner, *J. Electrochem. Soc.*, **97**, 139C (1950).
22. Rex Neihof and Karl Sollner, *J. Phys. & Colloid Chem.*, **54**, 157 (1950).
23. Walter Juda and W. A. McRae, *J. Am. Chem. Soc.*, **72**, 1044 (1950).
24. Rudolf Höber, *Physiol. Revs.*, **16**, 52 (1936).
25. T. Shedlovsky, *Science*, **113**, 2941 (1951).
26. Jacques Loeb, "Proteins and the Theory of Colloidal Behaviour," McGraw-Hill Book Co., Inc., New York (1922).
27. K. G. Denbeigh, "Thermodynamics of the Steady State," Methuen & Co., Ltd., London (1951).
28. K. S. Cole, *Proc. Nat. Acad. Sci.*, **35**, 558 (1949).
29. A. L. Hodgkin, *Biol. Rev. Cambridge Phil. Soc.*, **26**, 339 (1951).

DIFFUSION AND CONVECTION IN ELECTROLYSIS—A THEORETICAL REVIEW

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Introduction

Mechanisms of Ion Transfer

An electrode reaction proceeding at a finite rate involves movement of reacting materials between the electrode and the solution surrounding it. In absence of fluid turbulence, ions are transferred from solution to an electrode by three principal mechanisms: (*a*) migration, (*b*) diffusion, and (*c*) convection. For a given species the rate of transfer in the y direction per unit area perpendicular to y at any point in the fluid may be expressed by the equation:

$$N_t = cU\frac{\partial \phi}{\partial y} - D\frac{\partial c}{\partial y} + Vc \qquad [1]$$

where: N_t = total rate of transfer, gram ions/cm²-sec; c = concentration of given species, gram ions/cm³; U = mobility, cm²/sec-volt; ϕ = potential, volts; y = distance in direction of transfer, cm; D = diffusion coefficient, cm²/sec; and V = velocity of bulk fluid movement in direction of transfer, cm/sec.

The three terms on the right represent, respectively, the contributions of migration, diffusion, and convection. When transfer is not unidirectional corresponding equations may be written for each coordinate axis.

For unsteady state processes, changes of concentration with time must be considered, and the general transfer equation becomes (1)

$$\frac{dc}{dt} = -\operatorname{div}(Uc \operatorname{grad} \phi) + \operatorname{div}(D \operatorname{grad} c) - \vec{V} \operatorname{grad} c \qquad [2]$$

where t = time, sec. The potential ϕ must satisfy the Poisson equation (1), and the velocity vector $\vec{V}$ the three Navier-Stokes equations. Thus a set of nonlinear differential equations is obtained which has been solved only for a relatively few cases.

In a fluid in which turbulence has been induced by stirring or pumping, transfer by diffusion is augmented by eddy diffusion resulting from turbulent pulsations. Analytical solution of the convection-diffusion equations for such systems is in general impossible at the present time.

Equations for Steady State Mass Transfer

The term "mass transfer" will be used to denote the transport of ions or molecules by the combined effects of diffusion, eddy diffusion, and convection, excluding the contribution of migration to the process. The mass transfer process is commonly designated as "forced convection" when the system is mechanically agitated by stirring or pumping, and as "free convection" when mixing is induced as a result of density differences accompanying concentration differences from point to point within the fluid. Mass transfer in the steady state implies that the transfer rates, current density, concentrations, temperature, and other variables associated with cell operation are independent of time at any particular point in the system.

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The different mass transfer mechanisms participate to a varying degree as material moves from the main body of solution in contact with an electrode to the electrode-solution interface, with the nature of the process at any distance from the electrode depending on electrolyte motion, shape and position of the cell, and other operational variables. As a result of the participation of diffusion in the transfer process, it may be stated in general that movement of species toward or away from the electrode results in a decreasing concentration of the species in the direction of transfer.

For steady state processes it is convenient to express the rate of migration as a function of current per unit area perpendicular to the direction of transfer:

$$N_m = cU\frac{\partial \phi}{\partial y} = \frac{\Gamma I}{n\mathbf{F}} \qquad [3]$$

where: N_m = rate of migration, gram ions/cm²-sec; Γ = transference number for the given species; n = valence charge of the ion; and $\mathbf{F}$ = the Faraday, amp-sec/gram equivalent. In sufficient excess of inert electrolyte the transference number of the species participating in the electrode reaction may be made negligibly small and migration need not be considered. In the general case the rate of mass transfer may be expressed by the relation:

$$N_d = N_t - N_m = \frac{I(1-\Gamma)}{n\mathbf{F}}. \qquad [4]$$

Consider a cell containing at one end a vertical plane cathode upon which metal ions are being deposited. Assume that due to mechanical stirring the concentration is uniform at all distances from the floor of the cell at any particular distance x away from the electrode. For the species deposited a concentration profile through the main body of solution up to the electrode-solution interface may prevail as illustrated in Fig. 1. The exact shape of the profile will depend upon the mass transfer mechanism predominating at any place. Assume further that the concentration in the main body of solution remains constant. In view of the complicated nature of the problem it is sometimes convenient to express the over-all mass transfer process by equations of simple empirical form which relate the mass transfer rate to the difference between the mixed-mean or average concentration of the transferred species in the main body of fluid and the concentration at the electrode-solution interface.

(*A*) Mass transfer coefficient: the rate of transfer may be expressed by a coefficient, k_L, defined as follows:

$$N_d = k_L(c_b - c_i) \qquad [5]$$

where: N_d = mass transfer rate at any particular point on the electrode, gram mole/cm²-sec; k_L = mass transfer coefficient, cm/sec; c_b = average concentration in bulk fluid, gram mole/cm³; and c_i = concentration at interface.

(*B*) Equivalent film thickness or diffusion layer: this concept expresses the mass transfer process by the rate equation for steady state diffusion from concentration c_b to c_i over a hypothetical layer of stagnant fluid of thickness δ. The diffusional term of equation [1], i.e., Fick's first law, is

integrated for this case to give the relation which defines the equivalent film thickness:

$$N_d = \frac{D(c_b - c_i)}{\delta} \qquad [6]$$

where δ = equivalent film thickness.

This general mathematical formulation was originated by Nernst (2) who termed δ the "diffusion layer," a name which has been used widely throughout the electrochemical literature. The term "equivalent film thickness" has been used extensively in chemical engineering writings.

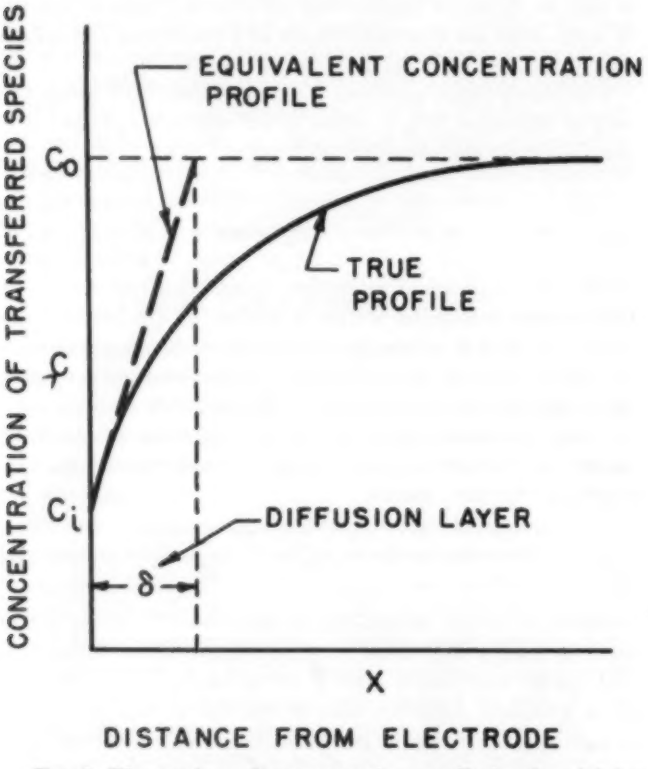

FIG. 1. Illustration of concentration profile in the vicinity of an electrode during electrolysis.

The relation between current density, concentration and electrode potential.—Taking the example of the deposition of an n valent metal in the presence of a large excess of "inert" electrolyte which takes no part in the electrode process, equation [6] can be expressed as:

$$\frac{I}{n\mathbf{F}} = \frac{D(c_b - c_i)}{\delta} \qquad [7]$$

The maximum rate of deposition, or *limiting current density*, will be given by the condition when $c_i = 0$, and

$$I_L = \frac{n\mathbf{F}D}{\delta} c_b. \qquad [8]$$

The current density can only be increased above this value if a consecutive electrode process is possible.

If one makes the assumption that δ is independent of the rate of diffusion, the concentration at the interface, c_i, can be related to the current density by combining equations [7] and [8],

$$\frac{c_i}{c_b} = 1 - \frac{\delta I}{Dn\mathbf{F}c_b} = 1 - \frac{I}{I_L}. \qquad [9]$$

Concentration polarization.—During the passage of current, the concentration of metal ions at the solution-electrode interface changes from the value at rest, c_b, to c_i. The corresponding shift in electrode potential, ΔE_c, the *concentration polarization*, is equal to the emf of a concentration cell with transference, in which the electrodes are in contact with solutions of concentrations c_b and c_i, respectively. If transference by migration of the potential determining ion is negligible and the ratio of ionic activity coefficients is assumed to be unity,

$$\Delta E_c = \frac{RT}{n\mathbf{F}} \ln \frac{c_i}{c_b}. \qquad [10]$$

The dependence of concentration polarization on current density for any current, I, can be found by combining equations [9] and [10]:[2]

$$\Delta E_c = \frac{RT}{n\mathbf{F}} \ln \left(1 - \frac{I}{I_L}\right). \qquad [11]$$

Unsteady State Diffusion

That concentration changes in solutions of electrolytes in the vicinity of working electrodes are of importance was realized as early as 1879 by Weber. In his work on the diffusion of zinc sulfate (3) Weber obtained an equation for the concentration as a function of time and distance from the electrode using a cell model of the form of a short cylinder closed at its ends by a cathode and anode and without liquid circulation or stirring. For practical calculations, use of this equation was not convenient since it contained a Fourier series which did not converge fast enough for large distances between the electrode and for small time periods.

In 1900, Sand (5) in an attempt to improve Weber's theory considered a model with only one electrode at the end of a semi-infinite cylindrical cell. Assuming no motion of the electrolyte, and the material transfer to occur only by diffusion, with the diffusion coefficient independent of concentration, equation [2] reduces to the form:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \qquad [12]$$

Upon integration of equation [12] with the boundary conditions as given below Sand obtained the result expressed by equation [13].

At $x = 0$, $\quad N_d = D \dfrac{\partial c}{\partial x}$; at $t = 0$, between $x = 0$ and $x = \infty$, $c = c_b$

$$c_{(x,t)} = c_b - \frac{N_d}{\sqrt{\pi D}} \int_0^t \frac{dt}{\sqrt{t}} \exp\left[\frac{-x^2}{4Dt}\right] \qquad [13]$$

where: $c_{x,t}$ = concentration at any time and distance x from the electrode; c_b = original uniform concentration; D = diffusion coefficient; N_d = rate of removal of ions at the electrode; and t = time.

For $x = 0$, i.e., at the electrode, this reduces to the simple equation:

$$c_{o,t} = c_b - 1.1285\, N_d \sqrt{\frac{t}{D}}. \qquad [14]$$

For a cathodic deposition N_d is given by equation [4].

[2] It should be noted that this expression applies only for electrodeposition. For discussions that include generalized electrode-reactions, and the effect of migration, see Ref. (4).

By means of equation [14] Sand was able to determine diffusion coefficients in electrolytes by observing the time interval necessary for a given current density to cause an ion depletion at the cathode to zero concentration, i.e., to reach limiting current density. Sand realized that this procedure is not rigorous on account of the variations in transference numbers with concentration. However, on the basis of Kohlrausch's work (6) he found that such variations result in an error not exceeding 2.5 per cent for the systems investigated.

An extension of the work of Weber and Sand was given by Rosebrugh and Miller in 1910 in an excellent paper on the mathematical treatment of electrolysis with direct and successive currents (7). A cell of uniform cross section provided with identical metal electrodes at both ends served as the model. The electrode reactions were assumed to be identical but opposite in sense (at the cathode, metal depositing; at the anode, metal going into solution, both with 100 per cent current efficiency).

Equation [12] was solved for the boundary conditions

$$\text{at } x = 0 \text{ (at half distance between the electrodes)} \qquad \frac{\partial c}{\partial t} = 0$$

$$\text{at } t = 0 \qquad \frac{\partial c}{\partial x} = 0.$$

Of most interest is the relation giving the concentration at the electrode as a function of time. Neglecting migration

$$\frac{D(c_b - c_i)n\mathbf{F}}{I \cdot L} = 1 - \frac{8}{\pi^2} \sum_{m=1,3} \frac{1}{m^2} e^{-m^2\eta t} \qquad [15]$$

where: $\eta = \frac{\pi^2 D}{4L^2}$, and L = half the length of the cell.

For $\eta t > 0.6$ equation [15] may be approximated by:

$$\frac{D(c_b - c_i)n\mathbf{F}}{I \cdot L} \cong 1 - \frac{8}{\pi^2} e^{-\eta t}. \qquad [16]$$

Similarly for $\eta t < 0.6$

$$\frac{D(c_b - c_i)n\mathbf{F}}{I} \cong 1.129 \sqrt{Dt}. \qquad [17]$$

Equation [17] shows the concentration at the electrode to be independent of the length of the cell. This result is identical to equation [14] indicating that for small ηt a cell of finite length can be treated as a semi-infinite column of electrolyte.

The foregoing equations have been found to agree fairly well with experimental findings (8, 9) for the deposition of a metal with the cathode placed horizontally at the top of the cell. In these experiments natural convection was suppressed.

Forced Convection

The treatment of an electrolytic cell as a slab of electrolyte free of convection currents, in which ions are transferred only by diffusion and migration, is not adequate to meet the conditions of actual operation.

Nernst (2, 10) and Brunner (11) developed the qualitatively correct concept of ionic mass transfer by the combined mechanisms of diffusion and convection. As a result of an elaborate experimental study of heterogeneous reaction rates Brunner developed the following argument.

During operation of an electrolytic cell, due to natural and forced convection the concentration in the bulk of the solution can be considered to be uniform. It may be assumed that a stagnant layer of electrolyte of thickness δ exists between the bulk of the solution and the electrode surface, across which mass transfer is possible only by diffusion and migration. The magnitude of δ depends only on hydrodynamic conditions (rate of stirring, rotation, etc.) and the viscosity of the solution.

In the steady state the concentration gradient in this "diffusion layer" is constant, and the rate of diffusion is equal to the rate of the electrode process. Thus for the case of metal deposition, equation [7] applies. For any particular solvent, geometry and rate of stirring, δ is a constant, and can be determined experimentally if $(c_b - c_i)$ and D are known. Under limiting current conditions $c_i = 0$, from which it follows that

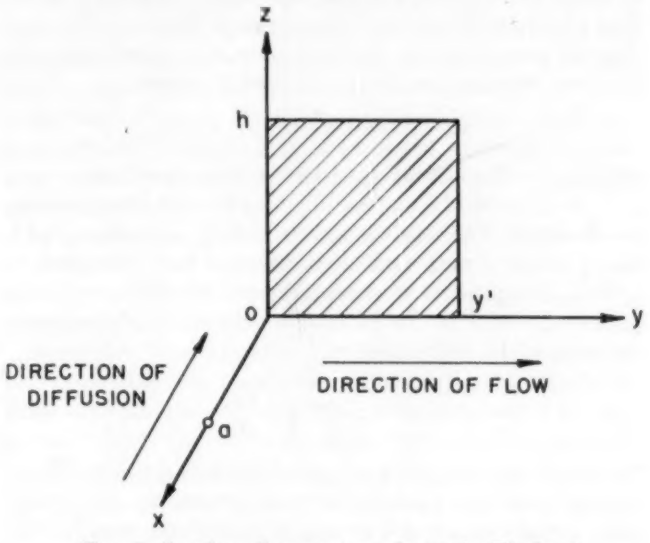

FIG. 2. Laminar flow past an electrode (Eucken)

$$\delta = \frac{n\mathbf{F}D}{I_L} c_b. \qquad [18]$$

Brunner (11) found that the thickness of the diffusion layer in some geometrical arrangements varied with the rate of stirring, and suggested the relation

$$\delta = \frac{a}{R^{2/3}} \qquad [19]$$

where: R = rate of stirring (rotation), rpm; and a = a constant for a given solvent, geometry, temperature.

In moderately stirred solutions in a number of experiments δ was found to be 0.02–0.05 mm (11, 12). Glasstone (13) suggested that $a = 0.05$ gives a fair agreement with experimental findings.[3]

Brunner realized that the assumption of a stagnant layer of electrolyte of δ thickness at the interface is physically incorrect. He also found that δ depends on the diffusion coefficient. His mass transfer experiments were carried out in a system of impractical geometry, and, therefore, only qualitative deductions can be made for different experimental conditions.

Methods of hydrodynamics were applied first by Eucken (14) to predict the effect of forced convection on mass transfer rates to electrode surfaces (Fig. 2). The limiting current in case of laminar flow in the y direction past an electrode of height h and width y_1 was evaluated for cases when the velocity of flow increases linearly with the distance from the electrode plane.

[3] In equation [19] δ is expressed in cm if used with $a = 0.05$. Conditions for application of this equation, such as rotor size, solution properties, etc., are not stated in reference.

Under steady state conditions the increase in concentration of a volume element $dx \cdot dy \cdot dz$ due to convection will be balanced by a decrease of concentration due to diffusion in a direction (x) perpendicular to the electrode.

By solving the differential equation for diffusion and convection

$$W_1 x^r \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial x^2} \qquad [20]$$

with the boundary conditions: at $x = 0$, $c = 0$; at $x = \infty$, $c = c_b$; where W_1 denotes the constant fluid velocity unit distance away from the electrode plane, the following expression was obtained for the total limiting current:

$$i_L = 77{,}800\, hc_b \sqrt[3]{D^2 y_1^2 W_1}\,. \qquad [21]$$

Dividing both sides of equation [19] by the surface area $A = h \cdot y_1$ yields the average limiting current density along the electrode. The result indicates that $I_{L\text{avg}}$ decreases with the ⅓ power of the length of the electrode in the direction of a flow, and increases proportionally to $D^{2/3}$. This conclusion is also supported by the expression obtained for the average thickness of the diffusion layer:

$$\delta_{\text{avg}} = 1.24 \sqrt[3]{\frac{Dy_1}{W_1}}\,. \qquad [22]$$

To obtain the simplified diffusion convection equation [20], Eucken made the assumption that no velocity component exists in the x direction. The results derived therefore may be of questionable value for practical applications (1). Eucken himself met with considerable difficulties trying to achieve such conditions in experiments designed to test equation [21] (30).

A fundamental approach to the solution of mass transfer problems based upon modern theories of fluid mechanics was initiated in the excellent series of papers by B. Levich (1, 15). The method involves application of the general equation for convection, migration, and diffusion (equation [2]), coupled with the Navier-Stokes equations for fluid motion and the Poisson equation for charge distribution in the solutions.

Levich succeeded in simplifying these nonlinear partial differential equations for the case of a binary electrolyte to the form

$$\frac{\partial c^*}{\partial t} + (\vec{V} \text{ grad})\, c^* = D\nabla^2 c^* \qquad [23]$$

where $c^* = \dfrac{c_1}{-n_2} = \dfrac{c_2}{n_1}$

and the effective diffusion coefficient

$$D = \frac{(n_1 - n_2)\, D_1 D_2}{n_1 D_1 - n_2 D_2}$$

$D_1 D_2$ = diffusion coefficients of ions 1 and 2, respectively;
$n_1 n_2$ = number of valence charges per ions of species 1 and 2, respectively;
c_1, c_2 = concentrations of ions 1 and 2, respectively.

Equation [23] from which the potential has been eliminated applies to the case of convective diffusion and determines for a known $\vec{V}$ the concentration at any time and point in the solution. Then the distribution of the potential is obtained from the distribution of the concentration by the equation:

$$\text{div } (c^* \text{ grad } \phi) = -\frac{RT(D_1 - D_2)}{\mathbf{F}(n_1 D_1 - n_2 D_2)} \nabla^2 c^* \qquad [24]$$

which upon integration yields:

$$\frac{\mathbf{F}^2}{RT}(n_1 D_1 - n_2 D_2)\, c^* \text{ grad } \phi + \mathbf{F}(D_1 - D_2) \text{ grad } c^* = -\frac{\vec{j}}{n_1 n_2} \qquad [25]$$

where $\vec{j}$ represents the vectors of current density and R = gas constant.

The solution of equation [25] allows the determination of the exact relation between the potential across the electrolytic cell and the current. This important separation of the convective diffusion from the potential distribution has been shown to be possible also for a tervalent system when the concentration of one kind of ions is low compared to that of the other two kinds.

A number of solutions for specific cases of definite geometric systems and hydrodynamic conditions were given as reviewed below.

A flat infinite disk rotating with a constant angular velocity.—Using von Karman's solution for the hydrodynamics of fluid motion about such a rotating disk the following result was obtained for steady state conditions in the discharge of one ion of a binary system:

$$\delta = 0.647 \left(\frac{D}{\nu}\right)^{\frac{1}{3}} \left(\frac{\nu}{Z}\right)^{\frac{1}{2}} \qquad [26]$$

where: δ = diffusion layer thickness (equation [6]); D = effective diffusion coefficient for the salt; ν = kinematic viscosity of the fluid; and Z = number of revolutions per second.

Thus for a system[4] with $D = 10^{-5}$ cm²/sec and $\nu = 10^{-2}$ cm²/sec

$$\delta = \frac{0.00647}{\sqrt{Z}} \text{ cm.}^4 \qquad [27]$$

Using the above value for δ, equations [8] and [11] may be utilized to give limiting currents or concentration polarization. Equivalent expressions are presented by Levich.

Flow past a flat electrode set into a laminar flow of liquid.—Levich developed a general theory of the laminar boundary layer by considering the analogy of the convective diffusion equation:

$$U \frac{\partial c}{\partial x} + V \frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \qquad [28]$$

to the Navier-Stokes equations for the velocity distribution.

The thickness of the diffusion boundary layer, δ, for the case of a flat electrode inserted into a laminar flow of fluid (16) is given for any distance x along the electrode by:

$$\delta = 3\left(\frac{\nu}{D}\right)^{-\frac{1}{3}} \left[\frac{\nu x}{U}\right]^{\frac{1}{2}} \qquad [29]$$

where U = velocity of the fluid and x = distance along the electrode from the leading edge.

For the case of the flat electrode equation [29] shows that for a given fluid velocity U the diffusion layer thickness increases as $x^{\frac{1}{2}}$, the square root of distance from the leading edge in the direction of fluid flow. This in turn affects the current

[4] In the original paper this equation is given as $\delta = \dfrac{0.022}{\sqrt{Z}}$ which appears to be in error.

stribution so that the local limiting current density $(I_L)x$ aries in the x-direction according to the equation:

$$(I_L)_x = \frac{n\mathbf{F}Dc_o}{\delta} = \tfrac{1}{3}\,n\mathbf{F}Dc_b\left(\frac{\nu}{D}\right)^{\frac{1}{3}}\left(\frac{U}{\nu x}\right)^{\frac{1}{2}}. \qquad [30]$$

his is valid if the flow past the electrode and the electrolysis egin at the same point. Upon integration for an electrode of idth b and length L the total limiting current is found to be:

$$i_L = \tfrac{2}{3}\,n\mathbf{F}Dc_b\left(\frac{\nu}{D}\right)^{\frac{1}{3}}\left(\frac{UL}{\nu}\right)^{\frac{1}{2}}b.^{5} \qquad [31]$$

It should be noted that the development of the Prandtl ydrodynamic boundary layer at the plate cannot go on definitely in an apparatus of finite size. How far in the x-diection its formation will extend, until a steady state boundary ayer of constant thickness is formed, depends not only upon he geometry of the entire cell (presence of any close parallel all, for instance) but also upon the length of the electrode. evich's equation [29] is acceptable from the hydrodynamical iewpoint only for a short electrode at a relatively low fluid elocity and in the absence of any close parallel boundary.

The problem of current distribution is also complicated. irst, because near an electrode edge submerged into an elecolyte the current distribution will be nonuniform and the quipotential surfaces by no means parallel to the electrode urface. Second, due to depletion of the ions, as the fluid oves along the electrode the electrode-potential changes ontinuously in the x-direction. This nonuniform potential , in turn, responsible for a nonuniform current distribution hroughout the electrode. These possible limitations should e considered in the general application of equations [30] nd [31].

Turbulent flow over a flat plate electrode.—Levich considered he boundary layer (region of disturbed velocity) developed ver the plate to be divided into three regions with respect o transfer of mass and momentum. In region 1, immediately djacent to the surface, turbulent pulsations are sufficiently lamped out so that transfer of momentum occurs by viscous hear and transfer of mass occurs by molecular diffusion. In egion 2, adjacent to region 1, turbulent pulsations are large nough to cause the transfer of mass to be predominantly by ddy diffusion or turbulent pulsations, but because of the elatively high kinematic viscosity of the liquid, momentum is ransferred predominantly by viscous shear. In region 3, the agnitude of turbulent pulsations is sufficient to cause transfer of both momentum and mass to occur by turbulent pulsaions. Within these assumptions by application of the mass nd momentum transfer analogy an equation was derived hich may be presented in the following expression for limitng current density:

$$I_L = \frac{n\mathbf{F}C_f u_o c_o}{2\left[A + (\alpha \mathrm{Sc}^{3/4} - A)B\sqrt{\frac{Cf}{2}}\right]} \qquad [32]$$

here: C_f = coefficient of resistance, or friction factor; $_o$ = velocity of flow past the plate; c_o = bulk concentration f transferred species; and A, B, α = constants to be evaluted experimentally. For turbulent flow over a flat plate t ordinary Reynolds numbers the coefficient of resistance is iven by:

$$C_f = 0.07\ \mathrm{Re}^{-0.2}$$

here Re = Reynolds number for flow.

[5] This equation is essentially equivalent to (12′), p. 287 in rigi al reference.

In general C_f depends upon the shape of the surface, roughness, and Reynolds number so that no complete generalization is possible.

As a more general relation for turbulent flow Levich suggests:

$$I_L = n\mathbf{F}C_f c_o u_o \varphi(\mathrm{Sc}, \mathrm{Re})$$

where: φ(Sc, Re) is a function which must be determined experimentally; Sc = ν/D, the Schmidt number.

Alternate expressions could be based upon the treatment of von Karman (6) for heat transfer. For low Schmidt numbers equation [32] agrees well with a formula obtained by Prandtl (18) for the corresponding case in heat transfer.

At high turbulence the thickness of the diffusion layer will be practically constant over most of the electrode, and the current and potential distribution will be correspondingly uniform.

In a subsequent paper (15) Levich extended the treatment of turbulent flow to nonstreamlined electrodes (cylinder placed perpendicularly to the electrolytic flow) and to electrodes of rough surfaces.

Along the lines suggested by Agar (19), Putnam, *et al.* (20) correlated limiting current densities for the inner electrode of an annular cell, with the mass transfer—heat transfer analogy. Mass transfer correlations were obtained in terms of equivalent film resistances using experimental data obtained from measurements with four different electrode reactions. The electrolytes were passed through an annular electrode system at various constant rates of flow. The experiments covered viscous and turbulent regions (Re = 59–30,000).

From the measured limiting currents and the inlet concentrations to the cell, the mass transfer coefficient was obtained as follows:

$$k_L = \left(\frac{(d_2^2 - d_1^2)}{4d_1 L}\right)\ln\frac{C_o}{c_i - 4I/n\mathbf{F}(d_2^2 - d_1^2)V} \qquad [33]$$

where: k_L = mass transfer coefficient; $d_1 d_2$ = diameter of inner and outer electrode, cm; L = length of electrode, cm; C_o = concentration of inlet stream gram mole/cc; I = limiting current, amp; n = number of electrons per molecule or ion reacted at the electrode; $\mathbf{F}$ = Faraday; and V = velocity cm/sec.

For the systems investigated in the *laminar flow* region the Leveque approximation (21) can be applied in the following form:

$$\frac{k_L d_e}{D} = 1.62\left(\frac{Gd_e}{\rho D_L}\right)^{\frac{1}{3}}\left(\frac{d_e}{L}\right)^{\frac{1}{3}} \qquad [34]$$

where: d_e = equivalent diameter, $d_2 - d_1$ cm; D = diffusivity, cm²/sec; G = mass velocity, gram/cm²/sec; and ρ = density of electrolyte, gram/cc.

The agreement of experimental data with the Leveque heat transfer equation was found to be satisfactory (within about ±3%).

The mass transfer under *turbulent flow* conditions was correlated in terms of the j_D parameter, defined by Chilton and Colburn (22) as:

$$j_D = \frac{k_L}{V}\left(\frac{\mu}{\rho D_L}\right)^{\frac{1}{3}} \qquad [35]$$

where V = velocity, cm/sec, and μ = viscosity, gram/cm/sec.

A satisfactory correlation of j_D as a function of Reynolds number was obtained. The function was found to agree

rather closely with the friction factor data of Carpenter, Colburn, and Wurster (23), i.e.,

$$j_D \approx \frac{f}{2} = 0.023 \left(\frac{d_e V \rho}{\mu}\right)^{-0.2} \quad [36]$$

where f = friction factor.

However, it is doubtful that great significance can be attached to this apparent agreement between momentum transfer and mass transfer in view of the high values of Schmidt numbers prevailing in liquid systems, and possible differences in surface roughness.

The correlation should be very useful in predicting mass transfer behavior in electrolytic cells, under flow conditions, in presence of a large excess of indifferent electrolyte.

Natural Convection

Natural convection or "spontaneous stirring" results when density changes accompany concentration changes in the region of the electrode. Fluid motion thus induced aids the mass transfer process by supplying fresh electrolyte from the bulk solution.

For a vertical plate electrode Levich (15) derived the following relation for the local limiting current density at any height X on the electrode surface:

$$(I_L)_X = 0.382\, n\mathbf{F}D \left(\frac{\nu}{D}\right)^{\frac{1}{3}} \left(\frac{g\alpha}{\nu^2}\right)^{\frac{1}{4}} X^{-\frac{1}{4}} c_b^{\frac{1}{3}} \quad [37]$$

where: α = density coefficient (defined by equation [38]); g = acceleration of gravity; and c_b = bulk concentration of species reacting.

The density coefficient, α, relates density changes to concentration changes:

$$\alpha = \frac{1}{\rho_b}\left(\frac{\partial \rho}{\partial c}\right) \approx \frac{\rho_b - \rho_i}{\rho_b(c_b - c_i)} \quad [38]$$

where ρ_b and ρ_i are fluid densities in bulk solution and at the electrode surface, respectively.

Equation [37] indicates that the limiting current density varies as the ¾ power of bulk concentration and inversely as the ¼ power of height on the electrode.

An alternate theoretical treatment has been presented by Wagner (24) who treated the electrolysis of a salt with a large excess of a "neutral" electrolyte ($CuSO_4$ with an excess of H_2SO_4). Wagner's derivation indicated the concentration of H^+ ions to increase at the cathode surface by ⅔ of the decrease of that of the Cu^{++}-ion, and the $SO^{=}_4$-ion concentration to decrease by the same factor. Using von Karman's (25) analysis of the boundary layer formed under free convection he derived for the limiting current density at the height X from the lower edge of the electrode

$$(I_L)_X = 4\mathbf{F}D(c_b)^{\frac{1}{3}} X^{-\frac{1}{4}} \left[\frac{g}{120 D_1 \nu} \frac{\partial \ln \rho}{\partial c_{CuSo_4}} - \frac{1.42^2}{3} \frac{\partial \ln \rho}{\partial c_{H_2SO_4}}\right]^{\frac{1}{3}}$$

or in a general form

$$(I_L)_X = 2n\mathbf{F}D(c_b)^{\frac{1}{3}} X^{-\frac{1}{4}} \left[\frac{g}{120 D\nu} \cdot \sum_1^j K_j \frac{\partial \ln \rho}{\partial c_j}\right]^{\frac{1}{3}} \quad [39]$$

where: D = diffusion coefficient of the species participating in the electrode reaction; c_b = bulk concentration of transferred component; ρ = density of the solution; and K_j = dimensionless constants calculated by equations analogous to [33] to [40] of the original reference.

Wagner obtained a fairly good agreement of his equation with experiments on a 0.1M H_2SO_4 system.

Natural convection has also been treated by Agar (1) who utilized a theoretical solution for the heat loss from a vertical plate derived by Schmidt, *et al.* (26) and obtained a result which may be expressed for limiting current density as follows:

$$(I_L)_X = 0.394\, n\mathbf{F}D \left(\frac{\nu}{D}\right)^{\frac{1}{3}} \left(\frac{g\alpha}{\nu^2}\right)^{\frac{1}{4}} X^{-\frac{1}{4}} Cb^{\frac{1}{3}}. \quad [40]$$

A further expression was derived by Keulegan (17), which yields for limiting current density:

$$(I_L)_X = 0.471\, n\mathbf{F}D \left(\frac{\nu}{D}\right)^{\frac{1}{3}} \left(\frac{g\alpha}{\nu^2}\right)^{\frac{1}{4}} X^{-\frac{1}{4}} c_b^{\frac{1}{3}}. \quad [41]$$

On the basis of experimental studies for deposition of $CuSO_4$ from sulfuric acid solutions the authors (27) have found the following equation to be applicable:

$$(I_L)_X = 0.505\, n\mathbf{F}D \left(\frac{\nu}{D}\right)^{\frac{1}{3}} \left[\frac{g(\rho_b - \rho_i)}{\rho_b c_b \nu^2}\right]^{\frac{1}{4}} X^{-\frac{1}{4}} c_b^{\frac{1}{3}} \quad [42]$$

where

$$\frac{\rho_b - \rho_i}{\rho_b c_b} = \alpha_{CuSO_4} - \alpha_{H_2SO_4} \Gamma_{H^+} \left[\frac{D_{CuSO_4}}{D_{H_2SO_4}}\right]^{\frac{1}{3}} \quad [43]$$

where α_{CuSO_4} and $\alpha_{H_2SO_4}$ = density coefficients for $CuSO_4$ and H_2SO_4 respectively; and Γ_{H^+} = transference number for hydrogen ion.

Thus it may be seen that all of the theories agree in essential form, differing primarily by a numerical constant. It should be noted that only equations [39] and [42] include the effects of migration of nonreacting species on the density difference established between the bulk solution and the interface.

The total limiting current density $(I_L)_{avg}$, at an electrode of height X_o is obtained by the relation:

$$(I_L)_{avg} = \frac{1}{X_o} \int_0^{X_o} (I_L)_X \, dx = \tfrac{4}{3} (I_L)_X. \quad [44]$$

Some authors (13) have attempted to treat free convection by assuming a constant diffusion layer thickness δ over the electrode of 0.05 cm. The foregoing theoretical analyses which have been substantiated by experimental evidence indicate, however, that δ depends on the electrolyte composition, viscosity, diffusion constant, density coefficient, and nature of the electrode reaction in regard to initiation of density changes, electrode height, shape, and orientation of the electrode in the solution. Unfortunately use of δ = 0.05 cm, which can lead to serious error in prediction of limiting currents, has been furthered in much of the subsequent literature on polarization phenomena and textbooks of electrochemistry (28, 29). The concept of diffusion layer with this numerical value is frequently presented without adequate qualification.

Conclusion

As described above, the early theoretical developments have at best provided treatment for ideal cases of diffusional supply to the electrode. The Nernst concept of a stationary diffusion layer was fruitful in this early period for a qualitative understanding of the mechanism of ionic transfer in the vicinity of the electrode. However, the diffusion layer concept is merely a convenient form for describing the mass transfer to the electrodes, and its thickness represents no real physical constant. Misunderstanding of this limitation has often led to erroneous interpretation of experimental work.

It is unfortunate that the theory of Prandtl's boundary ayer, patterns of velocity distribution, and other aspects of ydrodynamic theory have not been introduced into the field f electrochemistry until recently. Mass, heat and momentum ansfer analogies, and dimensional analysis are valuable ols in the development of modern theories of electrolysis. The use of concentration instead of activity in the electro-emical equations may lead to serious errors due to large anges of the activity coefficients with concentration. The rm of some equations, e.g., those accounting for diffusion ly, may still be acceptable if one merely considers the mbols for concentration as representing activity. However, hen mass transfer analogies are carried over to electrolysis, e distribution of concentration is obtained. Therefore, the ediction of the concentration polarization (which is a func-ion of the activities) is not possible unless the activity co-fficients are known for the entire range of concentrations. A further major difficulty arises from the fact that the meth-ds available at present for activity measurements yield e mean activity coefficients and not the activity coefficient f the potential-determining ion. The appreciation of these cts is essential for future theoretical and experimental evelopments in this field.

The variation of the diffusion coefficient with concentration ecomes a serious matter when high currents are applied. For his reason the validity of the now available relations for miting currents, derived with the diffusion coefficient as-med constant, is subject to question. For a given system e functional dependence of D on concentration can be tablished in general only by experiment. Such diffusivity easurements must be performed under conditions where nly the potential-determining ion diffuses under its own oncentration gradient.

In conclusion it may be stated that the recent developments hich have been reviewed in this paper represent a major ep toward establishment of quantitative theoretical methods r the prediction of mass transfer effects. This in turn should cilitate a more complete understanding of other aspects of ectrolysis.

REFERENCES

1. B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).
2. W. Nernst, *Z. physik. Chem.*, **47**, 52 (1904).
3. H. F. Weber, *Wied. Ann.*, **7**, 539 (1879).
4. J. N. Agar and F. P. Bowden, *Proc. Roy. Soc.*, **169A**, 206 (1938).
5. H. J. S. Sand, *Z. physik. Chem.*, **35**, 641 (1900).
6. B. Kohlrausch, *Wied. Ann.*, **62**, 209 (1897).
7. T. R. Rosebrugh and L. Miller, *J. Phys. Chem.*, **14**, 816 (1910).
8. L. V. Redman, *J. Phys. Chem.*, **29**, 548 (1925).
9. J. T. Burt-Gerrans, *J. Phys. Chem.*, **30**, 396 (1926).
10. W. Nernst, "Theoretische Chemie," 15th ed., p. 454, Enke, Stuttgart (1926).
11. E. Brunner, *Z. physik. Chem.*, **47**, 56 (1904).
12. W. Nernst and E. S. Merriam, *Z. physik. Chem.*, **53**, 235 (1905).
13. S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," pp. 81–85, Chapman and Hall, Ltd., London (1935).
14. A. Eucken, *Z. Elektrochem.*, **38**, 341 (1932).
15. B. Levich, *Acta Physicochim. U.R.S.S.*, **19**, 117 (1944).
16. B. Levich, *Disc. Faraday Soc.*, **37**, (1947).
17. G. H. Keulegan, *J. Res. Natl. Bur. Standards*, **47**, 156 (1951).
18. L. Prandtl, *Physik. Z.*, **29**, 487 (1928).
19. J. N. Agar, *Disc. Faraday Soc.*, **26** (1937).
20. C. S. Lin, E. B. Denton, H. S. Gaskill, and G. L. Putnam, *Ind. Eng. Chem.*, **45**, 2136 (1951).
21. J. Leveque, *Ann. mines*, **13**, 201 (1928).
22. T. H. Chilton and A. R. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).
23. E. G. Carpenter, A. P. Colburn, and A. Wurster, *Trans. Am. Inst. Chem. Engrs.*, **42**, 165 (1946).
24. C. Wagner, *J. (and Trans.) Electrochem. Soc.*, **95**, 161 (1949).
25. Th. von Karman, *Z. angew. Math. u. Mech.*, **1**, 244 (1921).
26. M. Ten Bosch, "Waermeuebertragung," p. 159, Springer, Berlin (1936).
27. C. R. Wilke, C. W. Tobias, and M. Eisenberg, paper presented before the Philadelphia Meeting of The Electrochemical Society, May 5, 1952.
28. S. Glasstone, "Introduction to Electrochemistry," pp. 445–458, D. Van Nostrand Co., Inc., New York (1942).
29. G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, pp. 400–408, Elsevier Publishing Co., New York (1951).
30. T. Tsukamoto, T. Kambara, and I. Tachi, *J. Electrochem. Assoc. Japan*, **19**, 311 (1950). (Subsequent to the preparation of this manuscript the author's attention was called to recent experimental and theoretical work dealing with the problem of the rotating electrode.)

A BRIEF SUMMARY OF HYDROGEN ELECTRODE KINETICS

J. O'M. Bockris[1]

I. Introduction

In recent years, many studies have been made of electrode kinetics. The hydrogen evolution reaction was once regarded as a particularly simple example of such kinetics, but in spite of the early date of the first publications (1, 2), the process is still not widely understood. A brief summary of this field is therefore given here.

II. Experimental Difficulties

Measuring Circuit Difficulties

Earlier workers often used commutators (3) to avoid resistance errors. These devices led to values of overpotential lower than the true ones. Although satisfactory commutators have now been made (4), their use (even at high current densities) is seldom advantageous unless resistive oxide films are present (5).

Effect of Trace Impurities

Attention was first drawn to the effects of trace impurities, e.g., tap grease, by Levina and Zarinskŭ (6) in 1937. These workers and others of Frumkin's school (7) used pre-electrolysis empirically to purify their solutions.[2] The nature and limiting concentration of impurities, and the conditions for satisfactory pre-electrolysis were not established. The concentration of impurities which first detectably affects reaction velocity was found by Bockris and Conway (10) in 1949 to be 10^{-10} gram mole/liter. "Catalytic poisons" such as As_2O_3 were the most effective. Traces of H_2S were shown to cause Tafel lines to deviate from linearity toward a limiting overpotential at high current densities. Conditions for pre-electrolysis and criteria of a "pure" solution were evolved (11).

Reproducible Preparation of Clean Metal Surfaces

Until recently, only mercury surfaces could be prepared in a clean state. Bockris and Conway (12) in 1948 satisfactorily sealed wire electrodes in hydrogen into thin glass bulbs, these being broken under the surface of the deoxygenated pre-electrolytically purified solution.

Parameters of electrode kinetics have been recently critically reviewed (13).

III. Reaction Paths

In aqueous acid solutions a proton approaching a cathode (M) during electrolysis undergoes

(*a*) Discharge:

$$H_3O^+ + e \rightarrow MH \qquad (I)$$

(*b*) Desorption:

either $$MH + MH \rightarrow 2M + H_2 \qquad (II)$$

or $$H_3O^+ + MH + e \rightarrow M + H_2 + H_2O. \qquad (III)$$

In alkaline solutions, possibilities are more numerous, particularly with mercury cathodes, where alkali metal cations may discharge (14). Two rejected mechanisms require comment. That involving prototropic transfer between water molecules (15) is improbable in acid solution because it gives a salt effect of incorrect sign and leads to an incorrect effect of hydrogen pressure on overpotential at constant current density. That involving discharge of the hydrogen molecule ion (H_2^+) is not acceptable because evidence concerning the stable existence of this ion is unsatisfactory (16).

In *pure* solutions, the kinetics may be complicated by (*a*) diffusion of atomic hydrogen into the bulk of the electrode and (*b*) the simultaneous existence of two reaction mechanisms. The first may cause time variation and is diminished by using thin wire electrodes; in Pd it is important and has received theoretical treatment (17). The second complication seldom occurs except over short ranges of current density (18).

IV. Dependence of Reaction Rate on Potential

Consideration of Part III shows that the over-all reaction in hydrogen evolution must be controlled by the rate of one of two *types* of reaction: (*a*) involving ions, or (*b*) involving atoms. The specific rate of reaction (II), of type (*b*), cannot be affected by electrical potential, for the chemical potential of its components depends only upon activity terms and the choice of standard states. Hence, the velocity of reaction (II) would be of the simple form $v_2 = ka_H^2$ where a_H is the activity of MH. The chemical potentials of the components in (I) and (III), reactions of type (*a*), depend on electrical potential, so that the velocities of (I) and (III) are potential dependent.

Consider a solvated proton at A (Fig. 1) before making its transition to the electrode, and assume that there is zero metal-solution potential difference. Then, the potential energy of activation is $(U_x - U_\infty)$. When a potential difference (e.g., electrode negative to solution) of $\Delta\phi$ exists between the electrode and the ions in the first layer on the solution side of the double layer, $(U_x - U_\infty)$ must be increased by the electrical work done on the charged particle initially at A in bringing it from A to the plane X. This is the potential difference between plane X and plane A multiplied by the charge on one proton, which, assuming a linear potential gradient, may be written $\beta\Delta\phi$, where

$$\beta = \frac{\text{horizontal distance } AX}{\text{horizontal distance } AB}$$

Hence, for transition from $A \rightarrow B$,

$$V_{A\rightarrow B} = K\, e(-\beta\Delta\phi\, e_o/kT) \qquad (IV)$$

where K is a constant containing $(U_X - U_A)$, concentration terms, etc.

Likewise, for transition from $B \rightarrow A$,

$$V_{B\rightarrow A} = K'\, e(1 - B)\Delta\phi\, e_o/kT. \qquad (V)$$

Equations of type (IV) and (V) were first obtained by Erdey-Gruz and Volmer (19) in 1930.[3] In 1935, Horiuti and Polanyi

[1] Imperial College of Science, London, England.

[2] Isolated examples of the use of pre-electrolysis, e.g., for purification of organic liquids and of aqueous solutions for use with reversible hydrogen electrodes (9) were previously known.

[3] For more detailed and rigid deduction see Ref. (20). Equations for cathodic and anodic currents *at equilibrium* as an exponential function of the potential were first deduced by Butler (21).

22) gave another deduction in which a coefficient similar to β arises as a function of the relative slopes of the intersecting Morse functions for the interactions $H_2O - H^+$ and $M - H$. This type of analysis has been developed into a quantitative method for theoretical calculation of the energetics of hydrogen evolution when reactions (I) (23) and (III) (24) are rate-determining.

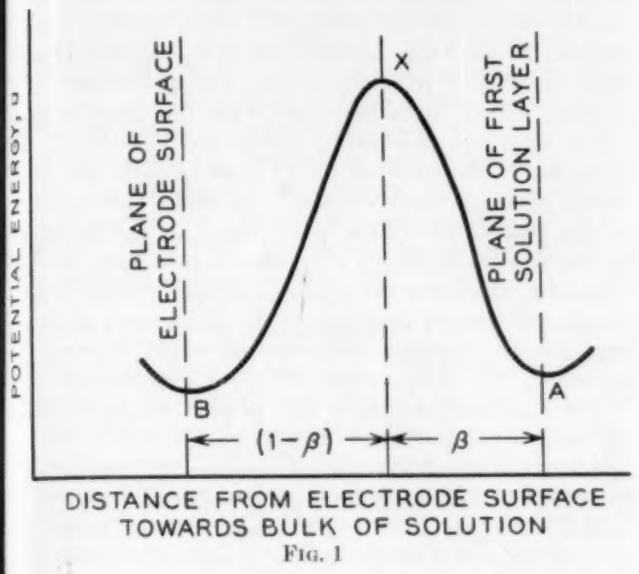

FIG. 1

V. Kinetics

From section IV, the following fundamental kinetic equations immediately follow ($\beta = \frac{1}{2}$)*

$$\vec{V}_1 = \vec{k}_1(1 - x)a_{H^+}\, e^{-\Delta\phi_e \mathbf{F}/2RT} \qquad \text{(VI)}$$

$$\overleftarrow{V}_1 = \overleftarrow{k}_1 x\, e^{\Delta\phi_e \mathbf{F}/2RT} \qquad \text{(VII)}$$

$$\vec{V}_2 = \vec{k}_2 x^2 \qquad \text{(VIII)}$$

$$\overleftarrow{V}_2 = \overleftarrow{k}_2(1 - x)a_{H_2} \qquad \text{(IX)}$$

$$\vec{V}_3 = \vec{k}_3 x a_{H^+}\, e^{-\Delta\phi_e \mathbf{F}/2RT} \qquad \text{(X)}$$

$$\overleftarrow{V}_3 = \overleftarrow{k}_3(1 - x)\, e^{\Delta\phi_e \mathbf{F}/2RT} \qquad \text{(XI)}$$

where k = velocity constant, a_{H^+} = activity of hydroxonium ions in the initial state of the indicated reaction, x = fraction of electrode covered with hydrogen atoms and a_{H_2} is the activity of molecular hydrogen. It would be desirable to evolve a quite general equation for the forward and backward components of the over-all reaction velocity, but such an equation is not mathematically amenable to the limiting cases corresponding to experimental results in pure solutions. Bockris and Potter (25) considered the kinetics of (I) followed by (II) and, separately, (I) followed by (III). By setting up the condition for constant coverage of the electrode with adsorbed atomic hydrogen at constant current density, one obtains an equation for x in terms of the rate constants of the various component reactions, and then expresses in these terms, and those of $\Delta\phi_e$ and a_{H^+}, the rate of the over-all reaction. Various special cases can be worked out by taking conditions corresponding to a particular step in the reaction sequences in (I) and (II) or (I) and (III), having a much higher energy of activation (with respect to some common reference state) than the other steps. Hence, equations for the relation between current density and potential corresponding to these various special cases (i.e., to what used to be called "theories of hydrogen overvoltage") can be obtained.

Equations thus obtained for the rate of the hydrogen evolution reaction at high overpotentials are of the form

$$i = K_j\, e^{\left[\frac{-\Delta G_j^*}{RT} - \frac{\alpha_j \eta \mathbf{F}}{RT} - \frac{\alpha_j \Delta\phi_R \mathbf{F}}{RT}\right]}, \qquad \text{(XII)}$$

where K_j is a constant, ΔG_j^* the free energy of activation corresponding to a slow stage j, $\Delta\phi_R$ the value of $\Delta\phi_e$ at the reversible potential (difference in inner potentials between metal and solution in absence of current flow), and α_j is a constant characteristic of j. K_j is easily evaluated; if ΔG_j^* and $\Delta\phi_R$ are known, approximate calculations can be made of the rate of the over-all reaction according to various j's and hence the most probable rate-determining reaction (the one giving the *fastest* over-all velocity under the given conditions) can be calculated. ΔG_j^* is approximately known by calculation (23, 26). $\Delta\phi_R$ is not known because of the contribution to it of surface potentials due to oriented solvent dipoles, overlap of metal electrons, etc. It is probable that these latter terms do not vary greatly between various metals (27); assuming this, $\Delta\phi_R$ can be expressed with respect to the potential of a charge-free surface and relative calculations for various metals made to determine mechanisms (24).

VI. Criteria of Mechanism

Formerly, when the problem of the kinetics of hydrogen evolution was referred to as the "theory of hydrogen overvoltage," it was common to attempt to "decide between the various theories" by carrying out qualitative experiments, e.g., effect of time on "growth of polarization," effect of state of surface, etc. (28). These experiments were abortive because they could usually be interpreted qualitatively in terms of several "theories." Also, the attitude which produced them was misleading as it suggested that hydrogen "overvoltage" was "caused" by a specific reaction, whereas it is more correct to regard all the reaction paths (I), (II), and (III) as occurring in hydrogen evolution, one of them being rate-determining. (The physical meaning of the hydrogen overpotential observed at a given current density is that, when multiplied by $\alpha\mathbf{F}$, it is the amount by which the free energy of activation of the reaction at the reversible potential has to be decreased to make the over-all reaction occur at the given rate.)

Consequently, it is preferable to concentrate on numerical criteria, which indicate the rate-determining mechanisms unambiguously.

Primary Criteria

Detailed theory shows that the most important criteria of the rate controlling reaction are[5]

$$(a) \qquad \frac{\delta\eta}{\delta \log i} = -2.303\frac{RT}{\alpha\mathbf{F}} = b,$$

when $e^{-\alpha\mathbf{F}/RT} > 10$ (see Table I).

* $\beta = \frac{1}{2}$ corresponds to a symmetrical energy barrier. Support for this assumption is given by (*a*) agreement between it and experiment in the *b* values obtained, (*b*) calculation of the Morse functions concerned (23).

[5] The relation between α and μ is $\alpha = 2\beta/\mu$. For a more detailed analysis of this relation, see Ref. (31).

(b) $$\mu = \frac{-2i_o\mathbf{F}}{RT}\left(\frac{\delta\eta}{\delta i}\right)_{\eta\to 0},$$

where $\left(\frac{\delta\eta}{\delta i}\right)_{\eta\to 0}$ is the limiting value of this quantity when $\eta \to 0$. A similar quantity to μ was first described by Horiuti and Ikusima (29) in 1939: μ (stoichiometric number) was first introduced into the general kinetics of hydrogen evolution, and its value thence deduced, by Potter in 1950 (30) (see Table I). The physical meaning of μ is "the number of times the rate-determining reaction must take place for one act of the over-all hydrogen evolution reaction to occur."

Values of b quoted as characteristic in Table I should be regarded as approximate (it having been assumed that $\beta = \frac{1}{2}$). In pure solutions, observed values vary little from those quoted. *Both* b and μ are, in general, necessary to decide upon mechanism, but observation of b values of 0.029 or 0.038 determines the mechanism without resource to μ determinations. The latter are difficult because of the low current densities at which measurements must be made to determine $(\partial\eta/\partial i)_{\eta\to 0}$. Note that μ determined by the above equation indicates the mechanism only at limitingly low current densities. For a discussion of the extension to higher current densities, see Ref. (32).

TABLE I. *Characteristic values of b and μ (25°C)*

Mechanism	b	μ
(I) slow, (II) fast	0.116	2
(I) fast, (II) slow	0.029	1
(I) slow, (III) fast	0.116	1
(I) fast, (III) slow	0.038 (low η) 0.116 (high η)*	1

* Condition for change, see Ref. (25).

Secondary Criteria

Determination of $(\partial\eta/\partial i)_{\eta\to 0}$ is difficult, particularly for metals of low i_o value (e.g., Hg, Pb, Sn) because of the degree of elimination of oxygen necessary. Two supplementary criteria may therefore be mentioned.

*p*H *and salt effects.*—These are used to distinguish the entity discharging, and to identify the ion undergoing discharge in alkaline solutions (14). Subsidiarily, the agreement between *p*H effect and theory (32, 33) provides information concerning parameters important in work on the structure of the double layer.

Heat of activation at the reversible potential.—This is of use in the calculations for distinguishing between mechanisms mentioned in Part V (25). Subsidiarily, it is a useful quantity with which to compare theoretical calculations concerning energy barriers involved in electrode kinetics.

When it is possible to determine the primary criteria, the mechanism of hydrogen evolution kinetics in pure solutions may be determined unambiguously. The requirement at present is the establishment of more data in highly purified solutions. For a summary of conclusions reached with data available up to 1951 see Ref. (25).

VII. Some Explanations

"Bonhoeffer Catalytic Anomaly"[6]

Bonhoeffer (34) showed that the rate at which hydrogen combined on metals fell into the same sequence as the hydrogen overpotentials at a given current density on these metals. This led some workers to conclude that (II) was the rate determining reaction for hydrogen evolution on all metals. This does not follow at all directly, however, because the reaction examined by Bonhoeffer possessed a mechanism in which combination occurred between an incident gaseous hydrogen atom and an adsorbed hydrogen atom (35). This is not the same as the mechanism (II), which is that of a radical reaction in which the substrate acts as a dissipator of energy upon collision of hydrogen atoms. The dependence of the reaction velocity upon the metal if the rate-determining reaction is (I) was explained by Horiuti and Polanyi (22). The minimum of the potential energy-distance curve for the adsorbed hydrogen atom resulting from discharge is a function of the heat of adsorption of hydrogen on the metal. The greater this is, the deeper the potential minimum, and, consequently, the lower the potential energy of activation for the proton transfer to the electrode. Hence, at a given current density, hydrogen overpotential would decrease with increasing heat of adsorption of hydrogen on the metal.

The apparent anomaly is that present results show that platinum is one of the few metals on which (II) is the slow reaction, at least at low current densities (36). According to Bonhoeffer, combination from the gas phase is fastest on Pt; anomalously, combination of hydrogen atoms is particularly slow on Hg, and it seems that the mechanism requires a fast (II) stage. This anomaly disappears if the effect of heat of adsorption on the rate of discharge is taken into account, and reaction (II) is regarded as only secondarily dependent on the nature of the substrate. For, on Pt, the heat of adsorption is large and hence discharge is particularly fast (37) so that the slower of the two stages is the recombination; whereas on Hg, with its much lower heat of adsorption of hydrogen, discharge is slower than the recombination reaction. A similar argument applies to the intervening series (38).

Trace Impurities

Results of "stoichiometric number" determinations for electrodes which adsorb hydrogen well suggest (32) that discharge of protons onto a metal such as Ni forms adsorbed atoms on a surface already highly covered with hydrogen atoms (or oxygen or hydroxyl from water). CO (a typical poison) can be adsorbed upon a nickel surface, leaving the remaining part of the surface unpoisoned so that hydrogen can still be adsorbed on it. Also, CO cannot displace adsorbed hydrogen from nickel (39). When traces of CO are adsorbed upon a cathode from solution, part of the (small) fraction of the surface still available for discharge is covered, so that the discharge step is decreased in rate. Hence, to maintain the same rate, the overpotential must be increased.

Let 10 mv (i.e., 5 mv = reproducibility) be arbitrarily considered an "appreciable" effect on hydrogen overpotential at a given current density. Calculation from the Tafel equation with $b \simeq 0.1$ shows that this increase in overpotential corresponds to a decrease in current density at constant overpotential of 25 per cent. From (VI), the current density is proportional to the free space on the electrode. Hence, the free space is reduced by 25 per cent. But, on nickel, discharge in pure solution occurs on a free space of only 20 per cent of the electrode area. Thus the fraction of the total surface area of the electrode covered with poison to cause an appreciable change is $0.2 \times 0.25 = 0.05$. The diameter of the CO molecule is about 3.8 Å. If n_c is the critical surface concentration of CO needed to cause appreciable poisoning, then,

$$n_c = \frac{0.05 \cdot 4}{\pi(3.8 \cdot 10^{-8})^2 \cdot 6.02 \cdot 10^{23}} \simeq 5.10^{-11} \text{ gram mole.}$$

[6] I am indebted to Dr. B. E. Conway for the suggestion of this appropriate name.

This compares reasonably with the surprisingly low experimental result (10).

Reversible Hydrogen Electrodes

A satisfactory reversible hydrogen electrode can be defined as an electrode the potential of which (*a*) follows the Nernst equation respective to activity of hydrogen ions under "practical conditions" (i.e., in relatively impure solutions), and (*b*) is not sensitive to the passage of small currents across it. To ascertain whether a given electrode material can be satisfactory as a reversible hydrogen electrode, we can calculate how much current it is necessary to pass in one direction so that its potential departs "appreciably" from the reversible value. Reversible cell measurements are usually made to an accuracy of about 1 mv. Hence let "appreciable" be taken as 1 mv. At low current densities (25),

$$i_c = -\lambda i_o \eta \mathbf{F}/RT, \qquad \text{(XII)}$$

so that at 25°C, with $\lambda = 1$ and $\eta = -0.001$ volt, $i_c \cong 5.10^{-2}\, i_o$, where i_c is the limiting current which can pass while the electrode still serves for 'reversible' ($\log i_o = a/b$, where a is the first constant of the Tafel equation). For Pt, $i_o \cong 10^{-3}$ and for Hg, 10^{-13}, so that a "hydrogen electrode" based on platinum will allow up to about $5 \cdot 10^{-5}$ amp/cm² across it while still remaining effectively reversible, but for Hg, currents greater than $5 \cdot 10^{-15}$ amp/cm² would destroy the reversibility. In practice, the most likely cause of stray electrode processes causing currents to pass across a hydrogen electrode is depolarization by oxygen, the limiting current for which is given by $i_l \cong 0.14c$ (40), where c is the concentration of oxygen in gram moles per liter. This is about 10^{-3} for a solution in equilibrium with air. On bubbling hydrogen through the solution, without taking special precautions to eliminate oxygen (i.e., a "practical" hydrogen electrode) we can reasonably assume the oxygen concentration reduced (at least) to 10^{-4} gram moles per liter. Hence, $i_l \cong 10^{-5}$ amp/cm². Thus, for a "practical" reversible hydrogen electrode

$$5 \cdot 10^{-2} i_o > 10^{-5}$$
$$i_o > 2 \cdot 10^{-4}.$$

This condition is fulfilled only by Pt and plated Au.

With increasing purity of the solution, more electrode materials become possible reversible hydrogen electrodes as the limiting currents i associated with the reaction between the electrode and impurities in the solution become less, the general condition[7] for effective reversible behavior being $i_o > 20 i_l$.

VIII. Electrode Kinetics in General

Many other electrode reactions may be less sensitive to impurities than is the hydrogen evolution reaction and not more complex theoretically, if allowed to take their simplest path. General electrode kinetics follows the model set by the hydrogen kinetics in being studied from two points of view: (*a*) that in which criteria of reaction mechanisms are deduced from current—potential relations [Erschler (41), Gerischer (42), Vetter (43), Parsons (31)]; and (*b*) that in which a detailed model is chosen and its statistical mechanical consequences worked out and compared with experiment.

Acknowledgment

I am indebted to Dr. D. C. Grahame for the stimulation needed to write this paper.

[7] The analysis given is approximate and neglects, for example, the possible formation of a chemisorbed oxide film on the electrode.

REFERENCES

1. H. Jahn and O. Schonrock, *Z. physik. Chem.*, **16**, 45 (1895).
2. J. Tafel, *Z. physik. Chem.*, **50**, 641 (1905).
3. E. Newbury, *J. Chem. Soc.*, **105**, 2422 (1914).
4. A. Hickling, *Trans. Faraday Soc.*, **33**, 1540 (1937).
5. J. O'M. Bockris and B. E. Conway, *J. Phys. Chem.*, **53**, 527 (1949).
6. S. Levina and V. Zarinskŭ, *Acta Physicochim. U.R.S.S.*, **6**, 491 (1937).
7. A. Frumkin, *Acta Physicochim. U.R.S.S.*, **18**, 23 (1943); *Disc. Faraday Soc.*, **1**, 57 (1947).
8. J. Schroder and E. Jaffe, *Ann. Physik*, **29**, 125 (1909).
9. A. H. W. Aten and M. Zieren, *Rec. trav. chim.*, **48**, 984 (1929).
10. J. O'M. Bockris and B. E. Conway, *Trans. Faraday Soc.*, **45**, 989 (1949).
11. A. M. Azzam, J. O'M. Bockris, B. E. Conway, and Hanna Rosenberg, *Trans. Faraday Soc.*, **46**, 918 (1950).
12. J. O'M. Bockris and B. E. Conway, *J. Sci. Instruments*, **25**, 283 (1948); E. C. Potter, *ibid.*, **29**, 160 (1952).
13. J. O'M. Bockris, *Natl. Bur. Standards (U. S.)*, "Electrochemical Constants" (1952).
14. J. O'M. Bockris and R. G. H. Watson, *J. chim. phys.*, **49**, 1 (1952).
15. H. Eyring, S. Glasstone, and J. Laidler, *J. Chem. Phys.*, **1**, 1053 (1939).
16. K. Hiroto and J. Horiuti, *Bull. Chem. Soc. Japan*, **13**, 228 (1938); A. Frumkin, *Inst. Phys. Chem. Research (Tokyo)*, **37**, 473 (1940).
17. A. Frumkin and N. Aladzhalova, *Acta Physicochim. U.R.S.S.*, **19**, 1 (1944).
18. R. Parsons, *J. chim. phys.*, **49**, 83 (1952).
19. T. Erdey-Gruz and M. Volmer, *Z. physik. Chem.*, **150**, 203 (1930).
20. R. G. H. Watson, Thesis, London, 1–21 (1950).
21. J. A. V. Butler, *Trans. Faraday Soc.*, **19**, 729 (1924).
22. J. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, **2**, 505 (1935).
23. R. Parsons and J. O'M. Bockris, *Trans. Faraday Soc.*, **47**, 914 (1951).
24. B. E. Conway, Thesis, London, 260–316 (1949).
25. J. O'M. Bockris and E. C. Potter, *J. Electrochem. Soc.*, **99**, 169 (1952).
26. R. Parsons, *Z. Elektrochem.*, **55**, 111 (1951).
27. H. Strehlow, *Z. Elektrochem.*, **56**, 119 (1952).
28. J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).
29. H. Horiuti and M. Ikusima, *Proc. Imp. Acad. (Tokyo)*, **15**, 39 (1939).
30. E. C. Potter, Thesis, London, 22–30 (1950).
31. R. Parsons, *Trans. Faraday Soc.*, **47**, 1332 (1951).
32. J. O'M. Bockris and E. C. Potter, *J. Chem. Phys.*, **20**, 614 (1952).
33. J. O'M. Bockris and B. E. Conway, *Trans. Faraday Soc.*, **48**, 724 (1952).
34. K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 213 (1924).
35. A. Schlechter, *Acta Physicochim. U. R. S. S.*, **10**, 379 (1939).
36. J. O'M. Bockris and A. M. Azzam, *Trans. Faraday Soc.*, **48**, 145 (1952).
37. P. Dolin, B. Erschler, and A. Frumkin, *Acta Physicochim. U. R. S. S.*, **13**, 793 (1940).
38. B. E. Conway, Thesis, London, 304–308 (1949).
39. O. Beek, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York (1950).
40. A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **37**, 319 (1941).
41. B. V. Erschler, *J. Phys. Chem. U. R. S. S.*, **22**, 683 (1948).
42. H. Gerischer, *Z. Elektrochem.*, **54**, 362 (1950); *ibid.*, **55**, 98 (1951).
43. K. Vetter, *Z. physik. Chem.*, **194**, 284 (1950); *Z. Elektrochem.*, **55**, 121 (1951).

MATHEMATICAL THEORY OF THE FARADAIC ADMITTANCE

(Pseudocapacity and Polarization Resistance)

David C. Grahame[1]

Introduction

Although it is relatively easy to measure the impedance of a metal surface in contact with an electrolyte, there has been no general agreement as to the significance of the results except in certain rather special cases, notably that of mercury in contact with inert electrolytes. Nevertheless the theoretical treatment of the subject can be made reasonably general without any assumptions about which there can be very serious doubt. To be sure, the theory to be presented deals only with smooth and homogeneous surfaces, which means in practice that it is quantitatively correct only for surfaces of liquid metals. But it is clear that no progress can be made in the study of the impedance properties of solid metals until this simpler problem is out of the way. Moreover it is reasonable to suppose that the solution of this problem will lead to a deeper understanding of metal-solution interfaces in general, which is the primary objective of all investigations of this sort.

It will not be necessary to assume in what follows that there exists a state of electrochemical equilibrium at the interface. The removal of this restriction broadens the scope of the argument and puts it in a different light from that of earlier treatments of the same problem. Thus it will not be necessary or convenient to speak of a potential-determining ion or of a potential-determining step, these being concepts which have no meaning in any but a state of equilibrium. Various aspects of the problem have been treated before, notably by Wien (1), Warburg (2), Krüger (3), Rosebrugh and Miller (4), Jones and Christian (5), Randles (6), Ershler[2] (7), and Gerischer (8). The present work is in agreement with the work of these authors, but presents the subject in a somewhat unusual manner and goes beyond earlier treatments.

General Considerations

Many persons who have worked on this problem in the past have attempted to represent the behavior of a metal-solution interface by means of an equivalent electrical circuit. The objection to this procedure is that one has no way of knowing whether or not a given equivalent circuit is, in fact, equivalent to the interface under consideration except by carrying out an independent analysis of the problem which it is the objective of those who use this method to avoid. It will be found, in fact, that in most instances no finite combination of resistors, condensers, and inductors can represent the variation with frequency of a metal-solution interface across which a current flows. Indeed, there is no reason to expect that it should be otherwise, except that we have not heretofore met a case where the equivalent circuit concept has been demonstrated to be fallacious.

[1] Department of Chemistry, Amherst College, Amherst, Massachusetts. The project of which this work is a part is supported by the Office of Naval Research.

[2] At the time this paper was written, Ershler's 1948 paper (in Russian) was not available to the author. Now a translation has been made (by Dr. R. Parsons, University College, Dundee), and it is found that Ershler's conclusions are not in disagreement with those drawn in this paper. The author wishes to express his gratitude to Dr. Parsons for making this translation available to him.

The impedance, Z, of a two-terminal network can be measured (usually, but not necessarily, with a bridge) as a function of three external variables, viz., the frequency of the (alternating current) test signal, the amplitude of that signal and the bias voltage or polarization. It is found in practice (and predicted from theory) that when the impedance is measured as a function of the amplitude of the input test signal, the impedance approaches a finite limit as the amplitude approaches zero. It is usually possible with the aid of rather simple electronic techniques to make measurements with so small an input signal that the directly measured value is not sensibly different from the limiting value. In the treatment which follows it will be assumed that this is done, or that a limiting process has been used to establish the true limit of the impedance at zero amplitude of the test signal. This makes it possible to regard the amplitude of the test signal as a vanishingly small quantity, which is the only case for which the mathematical analysis of the problem can be carried through.

Although it is possible in principle to obtain further information about a system by a study of the impedance as a function of amplitude, in practice it is not possible to do so for the reason just stated.

All known electrodes form nonlinear networks, which means that the impedance is a function of the bias potential (polarization). (This is why the impedance is a function of the amplitude of the test signal.) For this reason it is necessary to control the potential of the electrode relative to the solution in which it is immersed. The potential can be controlled either directly (through a device known as a potentiostat which automatically controls the potential by controlling the current) or indirectly by controlling the current. In the latter case, the potential will usually not be constant unless the solution is well "poised" (buffered with respect to its redox potential). It is a matter of indifference to the theory whether current or potential or neither is controlled. However, the theory only purports to give the variation with frequency of the impedance for an electrode in a constant state of polarization.

The theory to be developed below applies only to smooth homogeneous electrodes on which the current density (both a-c and d-c) is uniform. This means in practice that the two electrodes across which the current passes must be symmetrically disposed. Several kinds of symmetry are suitable, i.e., planar, cylindrical, or spherical. The last named gives the largest ratio of areas of the two electrodes, which makes it the most suitable when it is desired to consider the impedance properties of only a single electrode, namely the smaller one.

If the surface is not smooth and homogeneous, the current density will not be uniform. For reasons of geometry alone, a surface which is rough cannot be expected to have a uniform current density, and the difficulty is exaggerated by the fact that a rough surface will probably be chemically inhomogeneous as well, so that the electrochemical reaction may well favor certain catalytically active spots.

The manner in which diffusion effects are to be taken into account needs to be explained. There are two slightly different kinds of diffusion effects to be considered. First there

are those which arise as a result of the passage of the steady direct current, and second, there are those which arise as a result of the very small alternating current. The former will be left out of account on the grounds that it is the task of the experimenter to control or at least to know the concentrations of the reactants at the interface under the conditions of the experiment, apart from those which are caused by the alternating current. Even if they are not known, they can be held constant during a succession of impedance measurements in which the only variable is the frequency of the alternating current, and it is this variable with which the present theory is concerned.

The effects of diffusion arising from concentration changes associated with the flow of alternating current, although very small and in the limit zero, cannot be neglected because the ratio of concentration changes to current changes does not necessarily (or actually) go to zero in the limit, and it is this ratio which determines the impedance of the electrode, apart from the impedance of the electrical double layer.

I. The Double Layer Impedance

There are two ways in which the current is carried across the interface of a metal-electrolyte system, and these two may be called the faradaic and nonfaradaic paths, respectively. In the former, current crosses the interface by virtue of an electrochemical reaction such as the reduction or oxidation of water or of some ion. In the latter (nonfaradaic) case charged particles do not cross the interface, and the current is carried by the charging and discharging of the electrical double layer, which behaves like a condenser in series with the ohmic resistance of the solution.[3]

[3] A possible ambiguity needs to be considered here. How is one to differentiate between a faradaic and a nonfaradaic current? The answer is that any process which allows a continuous current to flow will be regarded as faradaic, whereas one which does not will be regarded as nonfaradaic. An equivalent but slightly more fundamental definition will be given in section II.

The question of whether or not a continuous current flows hinges upon the question of whether or not the products of electrolysis can build up in concentration (or more strictly in chemical potential) in such a manner as to stop the flow of current. If one or more of the products of electrolysis can diffuse away, this will never happen, since more current will be needed to replace the substance which has diffused away. Likewise if the product of electrochemical action is capable of undergoing a second reaction by which its concentration (chemical potential) is lowered, a faradaic current will flow to replace the substance used up in the chemical reaction. (This happens when hydrogen atoms combine to form hydrogen molecules.) Finally, a faradaic current will flow if the product of reaction has a natural upper limit of chemical potential which is reached before the counterelectromotive force needed to stop the reaction is attained. This happens very often in electrochemical processes, as in the deposition of a metal or the formation of an insoluble salt with the metal of the electrode. The evolution of a gas at an electrode is usually not an example of this effect, however, since the production of gaseous molecules does not ordinarily occur in a single electrochemical step.

This discussion also bears upon the question of the distinction between an adsorbed ion and an ion which has acquired or lost electrons to become an atom. Even the adsorbed ion is associated with an equal amount of the opposite charge in the double layer, so that the distinction cannot be made simply on the basis of the charge. The distinction is made on the basis of whether or not the adsorption is such as to allow a continuous current to flow, as discussed above. Thus if the "adsorbed" ion together with its associated charge can diffuse away from the interface as a unit, the ion has really reacted with the charge. Likewise, if the adsorbed ion has formed a soluble or insoluble salt with the metal, thereby exposing more metallic surface and allowing more current to flow, the ion has in fact reacted and is not to be considered adsorbed.

Since the total current is by definition the sum of the faradaic and nonfaradaic components, it is convenient to regard the interface as electrically equivalent to two impedances in parallel. The nonfaradaic impedance is then that of the electrical double layer and may be represented as a simple capacitance in so far as its variation with frequency is concerned (7, 9).[4] The faradaic impedance, on the other hand, is not representable in any such simple fashion. It is the purpose of this paper to find out how large it is and how it varies with frequency and to devise a method of representing that variation in an easily intelligible fashion. Equivalent circuits will be written down only after these properties have been deduced.

It is sometimes convenient to think of the faradaic impedance as an admittance[5] shunting the capacitance of the double layer.

Before beginning that task it is necessary to examine the influence of the concentration changes caused by the faradaic and nonfaradaic impedances. There are four effects to be considered, since each of the two causes of concentration change affects each of the measured impedances. These will be considered in turn.

Effect of the concentration changes produced by the nonfaradaic current upon the measured capacity of the electrical double layer.—This matter has been dealt with by the author elsewhere (9) and only the qualitative results will be repeated here. It is found that the effect is extremely small, but not zero, even in the limit as the amplitude of the alternating current approaches zero. A small polarization *resistance* also appears, but is less than the error of measurement in all cases so far considered. No appreciable error is to be anticipated, therefore, as a result of neglecting this effect altogether. In a sufficiently refined treatment, however, the equations for making the necessary corrections are available.

Effect of the concentration changes produced by the alternating component of the faradaic current upon the capacity of the double layer.—Note that when we speak of the capacity of the double layer we mean the capacity associated with the nonfaradaic current. The effect of the alternating component of the faradaic current upon the capacity of the double layer has not yet been investigated theoretically. It is evident that the effects will be of the same order of magnitude as those produced by the nonfaradaic current as long as the faradaic current is itself of the same order of magnitude as the nonfaradaic current. In that case the effects will be negligible. And if the faradaic current becomes large, the faradaic admittance will be so large that small errors in the computation of the nonfaradaic admittance (the capacity of the double layer) will be altogether negligible. So there seems to be no reason to make a more detailed study of this effect.

Effect upon the measured faradaic admittance of concentra-

[4] This conclusion is based chiefly upon the results of work done with mercury. However, it is observed that the capacity of other metal electrodes in contact with inert electrolytes reaches a finite limit at high frequencies, which shows that at least a part, and generally the major part, of the capacity of the double layer is frequency-independent.

[5] Admittance is the reciprocal of impedance. The faradaic admittance is, therefore, that part of the admittance attributable to electrochemical changes at the interface.

tion changes produced by the nonfaradaic current.—This is an effect which can and will be included in the differential equations to be written later. By a suitable choice of experimental conditions it is often possible to eliminate the effect: There is no theoretical reason for believing that the effect will otherwise be small, however, since the concentration changes produced by the nonfaradaic current will usually be at least as large as those produced by the alternating component of the faradaic current.

Effect upon the faradaic admittance of concentration changes produced by the alternating component of the faradaic current.—This is the effect with which this paper is primarily concerned.

There is one further effect which is not considered in this paper and that is the liquid junction potential or diffusion potential produced at the interface as a result of the concentration gradients set up there. This effect is of the same order of magnitude as the second effect listed above, and if it were not so, it should appear also in measurements of the capacity of the electrical double layer on mercury. Thus we conclude that it is justifiable to neglect it in the present treatment.

Relation of the Double-Layer Admittance to the Faradaic Admittance

The admittance of the double layer adds to the faradaic admittance, which is why it is proper to think of the two admittances as impedances in parallel. We now develop the equations expressing this relationship, principally for use in later sections.

Let the faradaic current be denoted by i. It is made up, in general, of a steady current i_o and a sinusoidal component $a \sin \omega t$.

$$i = i_o + a \sin \omega t. \qquad [1]$$

It may be mentioned in passing that the study of a current composed of a steady part and *two* sinusoidal components of different frequencies adds nothing to the understanding of the problem either experimentally or theoretically. The effects are merely additive throughout.

The nonfaradaic current will not in general be expected to have either the same phase or the same amplitude, and it will have no steady component, in agreement with our definition of the nonfaradaic current. Its frequency will naturally be the same. Calling the nonfaradaic current i_{di} we have

$$i_{di} = b \sin (\omega t + \delta) \qquad [2]$$

where δ is the unspecified phase angle and b is the small (and in the limit zero) amplitude of the alternating nonfaradaic current.

In operating an impedance bridge it is possible to determine the vector impedance either in terms of the equivalent *series* resistance and reactance (here the reactance is always a capacitance) or in terms of the equivalent *parallel* resistance and reactance. It is much more convenient to carry through the mathematical derivations for the equivalent *series* circuit, although the results have nothing to do with this choice.

The series resistance R_s and series capacitance C_s (Ershler's $\overline{R}_R$ and $\overline{C}_R$), whose impedance at the frequency in question matches that of the interface under test, generate an instantaneous potential whose change with time, dE/dt, is

$$dE/dt = R_s\, di_t/dt + (i_t - i_o)/C_s \qquad [3]$$

where i_t is the total current and where the last term on the right will be recognized as a rearrangement of the familiar equation $C_s = dQ/dE = i dt/dE$. From equations [1] and [2] and noting that $i_t = i + i_{di}$

$$di_t/dt = a\omega \cos \omega t + b\omega \cos \delta \cos \omega t - b\omega \sin \delta \sin \omega t \qquad [4]$$

and, therefore

$$dE/dt = a\omega R_s \cos \omega t + b\omega R_s \cos \delta \cos \omega t - b\omega R_s \sin \delta \sin \omega t + (1/C_s)(a + b \cos \delta) \sin \omega t + (b/C_s) \sin \delta \cos \omega t. \qquad [5]$$

Regarding the electrical double layer as a condenser of capacity[6]

$$C,\ dE/dt = (b/C) \sin (\omega t + \delta) = (b/C) \cos \delta \sin \omega t + (b/C) \sin \delta \cos \omega t \qquad [6]$$

and by comparison with equation [5], equating terms in $\sin \omega t$ and $\cos \omega t$

$$a/C_s + (b/C_s) \cos \delta - b\omega R_s \sin \delta = (b/C) \cos \delta \qquad [7]$$

$$a\omega R_s + b\omega R_s \cos \delta + (b/C_s) \sin \delta = (b/C) \sin \delta. \qquad [8]$$

Since a and b are arbitrarily small, only their ratio is significant. Let $q = a/b$; then

$$q\omega R_s + \omega R_s \cos \delta + (1/C_s) \sin \delta = (1/C) \sin \delta \qquad [9]$$

$$q/C_s + (1/C_s) \cos \delta - \omega R_s \sin \delta = (1/C) \cos \delta. \qquad [10]$$

These equations can be solved for δ and q giving

$$\tan \delta = C_s\zeta/(C_s - C - \zeta^2 C) \qquad [11]$$

$$q = [(C_s - C)/C] \cos \delta + \zeta \sin \delta \qquad [12]$$

where $\zeta = R_s C_s \omega$.

These equations make it possible to find δ and q from an experimental measurement of C_s and R_s, assuming C already known. C is the ordinary differential capacity of the electrical double layer, which can be found, for instance, by taking measurements at a series of high frequencies and extrapolating the observed value of C_s to infinity. This amounts to assuming that the capacity of the double layer is independent of frequency and that the faradaic impedance does not fall off with increasing frequency as rapidly as does the impedance of the double layer, a result confirmed by the theory to be developed below. These assumptions have nothing to do with the validity of equations [11] and [12], of course.

In a typical case (Pt in H_2SO_4), the details of which need not concern us here, measurements made at 1000 cycles revealed that $\delta = 21°$ and $q = 0.22$. These are typical values for metals other than mercury. Evidently 22/122 = 18 per cent of the alternating current produced chemical changes and the rest, 82 per cent, went to the charging and discharging of the electrical double layer. The two currents were 21° out of phase and thus were not in quadrature, as certain too simple theories might have led one to expect.

If the faradaic current were a function of the potential difference across the interface and of that alone, then the faradaic admittance would be represented by a pure resistance, and the phase angle δ would equal $\pi/2$ at all frequencies. This is contradicted by experiment, as mentioned above, and shows that the faradaic current is affected by the concentrations of the reactants and products of electrolysis (or at least of some substance present at the interface whose concentration depends upon the alternating faradaic current).

[6] It is not strictly necessary to regard the electrical double layer as a pure capacitance in this derivation, and if cases should be found in which it was not, the derivation would not be significantly altered in its conclusions. However, the experimental task of evaluating the faradaic admittance would then become very formidable indeed.

This result serves to illustrate the possible applications of equations [11] and [12]. It must be mentioned, however, that the method used in the above example depends upon the assumption that the electrode used was smooth and homogeneous. This was probably not so, with the result that the values quoted cannot be taken to be quantitatively significant. They are almost certainly reliable enough to support the qualitative conclusions drawn, however.

Because the impedance (or admittance) of the double layer can be subtracted from the total admittance in a simple manner, it will be unnecessary to carry it in the equations which follow. Thus in the remaining parts of this paper R_s *and* C_s *will denote the equivalent series resistance and capacitance of the* faradaic *admittance alone*, it being understood that the admittance of the double layer is electrically in parallel with it. With this understanding it will be necessary to rewrite equation [3], putting i in place of i_t, so that we have

$$dE/dt = R_s\, di/dt + (i - i_o)/C_s \qquad [13]$$

or from equation [1] (which remains valid)

$$dE/dt = a\omega R_s \cos \omega t + (a/C_s) \sin \omega t. \qquad [14]$$

These are the only equations from this section needed in the parts which follow.

II. General Expressions Relating Voltage to Current

It is intended to develop the theory of the faradaic admittance in as general a manner as possible, isolating from the main argument all assumptions of a doubtful or special character. The treatment here to be employed asserts as a truism that the faradaic current, i, is a function of E,[7] the potential across the interface, and of the concentrations v_o', w_o', y_o', etc., of V, W, and Y, respectively, *at the interface*, i.e., within the double layer itself.[8] Mathematically expressed

$$i = f(E, v_o', w_o', y_o', \text{etc.}). \qquad [15]$$

The substances whose concentrations are to be included in the list of variables are those whose concentrations are independently variable in the sense of the phase rule. Although electrical neutrality is not preserved in the electrical double layer, the total charge is not independently variable, so that one charged component must be regarded as a dependent variable. It should be noted that the products of electrolysis are components of the system, even if they are not initially present.

Each concentration v_o', w_o', etc., is itself a function of the potential E and of the *volume* concentrations of all of the independently variable components at the interface. These latter concentrations will be called v_o, w_o, etc., and denote the concentrations of V, W, etc., at a distance from the interface just exceeding that at which the effect of the double layer begins to be appreciable. More precisely, they are extrapolated concentrations representing the expected values at the interface if the electrical double layer were absent. From what we have just said

$$v_o' = f(E, v_o, w_o, y_o, \text{etc.})$$
$$w_o' = f(E, v_o, w_o, y_o, \text{etc.})$$
$$y_o' = f(E, v_o, w_o, y_o, \text{etc.})$$
$$\text{etc.}$$

It will be understood that the three functions are not the same, even though we have used the same symbol f for all three. A similar remark applies to equations [15a] and [15b] below. These equations depend for their validity upon the supposition that the electrical double layer remains at equilibrium with the layers of electrolyte in its immediate vicinity, that is, at distances comparable to the half-thickness of the double layer itself. It is known from experiment (14) that there is no detectable lag (less than a microsecond) in the charging of the electrical double layer, and this also follows immediately from the theory of the double layer. Thus it is safe to conclude that the composition of the electrical double layer is a unique function of the composition of the electrolyte adjacent to it and of the potential existing across it.

It follows that the faradaic current is also a function of E, v_o, w_o, y_o, etc.

$$i = f(E, v_o, w_o, y_o, \text{etc.}). \qquad [15a]$$

Equation [15a] will be rewritten in the equivalent form

$$E = f(i, v_o, w_o, y_o, \text{etc.}) \qquad [15b]$$

from which it follows from the principles of calculus that

$$dE/dt = (\partial E/\partial i)di/dt + (\partial E/\partial v_o)dv_o/dt + (\partial E/\partial w_o)\, dw_o/dt + \cdots$$

which will be written for short

$$dE/dt = \theta\, di/dt + \beta\, dw_o/dt + \gamma\, dv_o/dt + \cdots \qquad [16]$$

where

$$\theta = (\partial E/\partial i)_{v_o,\, w_o,\, \text{etc.}}; \quad \beta = (\partial E/\partial w_o)_{i,\, v_o,\, \text{etc.}};$$
$$\gamma = (\partial E/\partial v_o)_{i,\, w_o,\, \text{etc.}} \qquad [17]$$

The subscripts have been added in equation [17] to emphasize the meaning of the partial differential coefficients. Introducing equation [1] puts equation [16] into the form:

$$dE/dt = \theta\, a\omega \cos \omega t + \beta\, dw_o/dt + \gamma\, dv_o/dt + \cdots \qquad [18]$$

Then equating dE/dt in equations [14] and [18] yields

$$a\omega R_s \cos \omega t + (a/C_s) \sin \omega t = \theta\, a\omega \cos \omega t + \beta\, dw_o/dt + \gamma\, dv_o/dt + \cdots \qquad [19]$$

The plan of procedure now is to evaluate dw_o/dt, dv_o/dt, etc., by the use of the appropriate diffusion equations and so to permit the evaluation of R_s and C_s from equation [19]. Before proceeding with this plan, however, an important consequence of equation [19] needs to be noted.

The quantities dw_o/dt, dv_o/dt, etc., will in general be functions with terms in cos ωt and in sin ωt. Then equating coefficients of these terms one will obtain equations of the form

$$R_s = \theta + f_w(\beta, dw_o/dt) + f_v(\gamma, dv_o/dt) + \cdots \qquad [20]$$

$$1/C_s = g_w(\beta, dw_o/dt) + g_v(\gamma, dv_o/dt) + \cdots \qquad [21]$$

[7] By E we shall mean not the potential from the metallic phase to either the inner or outer Helmholtz plane but the potential across the entire double layer, exclusive of any IR drop that may occur in case the double layer is so thick that this is appreciable. With this definition of E, equation [15] is not altogether axiomatic, since it contains a hidden assumption to the effect that the potential drop across the diffuse double layer is itself a function of the same variables as those listed. This would seem to be certainly true if current ideas about the electrical double layer are at all correct.

[8] More precisely these primed quantities are the concentrations at the plane of closest approach of the substances in question. It may be mentioned that we here use the word "substance" to include ions. It should also be mentioned that there is one class of substance (discussed under class I below) for which it is necessary to define v_o', w_o', etc., as activities rather than concentrations. The substances in question are not ions.

where f_w and g_w are functions obtained by solving a differential equation subject to appropriate limiting conditions *all relating to a particular substance*, W. In a like manner f_v and g_v are functions relating to a particular substance, V, and so on. That is to say, the faradaic admittance (which is now more easily thought of as an impedance) is representable as a series combination of resistances and capacitances, each referring to a particular substance in the system. More precisely, the faradaic impedance is representable as a series combination of a resistance θ and a series of characteristic impedances, one for each substance in the system (except that many turn out to be zero). The resistance θ turns out to be simply related to the exchange current at equilibrium, as explained below, and the characteristic impedances are for the most part not representable in their variation with frequency by finite combinations of ordinary R's, C's, and L's.

It will be convenient to classify substances according to the differential equations which they must satisfy. Substances in the same class can be lumped together in the final representation of the equivalent circuit, which results in a worth-while simplification. In Part III, which follows, a number of the more important cases are listed, and in Part IV the appropriate differential equations are set up and solved.

Without going further, it is possible to evaluate θ from certain rather well established principles of reaction kinetics. According to these, $\vec{i}$, the rate of the forward electrochemical reaction, is given by

$$\vec{i} = n\mathbf{F}w_1k_1 \exp(\alpha n\mathbf{F}E/RT) \qquad [22]$$

and $\overleftarrow{i}$, that of the backward reaction, by

$$i = n\mathbf{F}w_2k_2 \exp[-(1 - \alpha)n\mathbf{F}E/RT] \qquad [23]$$

where w_1 and w_2 are the concentrations of the reacting species at the interface, k_1 and k_2 are specific reaction rate constants whose magnitudes depend upon the zero of the scale of potentials chosen for the representation of E, the potential across the interface. It proves to be unnecessary to stipulate where this zero lies, which is fortunate in view of the fact that this is the one respect in which equations [22] and [23] may be said to be debatable. The transfer coefficient α represents the fraction of the potential E which acts to facilitate the forward (discharge) reaction. In the same way $1 - \alpha$ represents the fraction of the potential which acts to retard the reverse reaction. n is the number of electrons involved in the elementary act of reduction or oxidation.

The net current at any potential is

$$i = \vec{i} - \overleftarrow{i} \qquad [23a]$$

and hence

$$\partial i/\partial E = (w_1k_1\alpha n^2\mathbf{F}^2/RT) \exp(\alpha n\mathbf{F}E/RT) + [w_2k_2(1 - \alpha)n^2\mathbf{F}^2/RT] \exp[-(1 - \alpha)n\mathbf{F}E/RT] \qquad [24]$$

and therefore

$$\partial i/\partial E = (n\mathbf{F}/RT)(\alpha i + \overleftarrow{i}) = 1/\theta. \qquad [25]$$

θ has been introduced by means of its defining equation [17]. If θ and α are known experimentally, equation [25] gives all that is needed for the evaluation of $\vec{i}$ and $\overleftarrow{i}$, quantities whose evaluation has long been regarded as much to be desired [13].

At the equilibrium potential it is not even necessary to know α, since then i is zero. For this special case one has

$$\vec{i}_{eq} = \overleftarrow{i}_{eq} = RT/n\mathbf{F}\theta \quad \text{or} \quad \theta = RT/n\mathbf{F}\vec{i}_{eq} \qquad [26]$$

which is identical with a result obtained by Dolin and Ershler (7, 17) and used extensively in the Russian work on hydrogen overvoltage (13, 15, 17–20). It is also a more compact form of Randles' equation [18] (6). To show that this is so we begin by quoting Randles' result, namely

$$R_r - \frac{1}{\omega C_r} = \frac{RT}{n^2\mathbf{F}^2.1Ck}$$

where R_r is the equivalent series resistance after the capacity of the electrical double layer has been subtracted out in the proper vectorial manner; $1/\omega C_r$ is the impedance of a condenser which corresponds to the capacitative part of the Warburg impedance (see below). Since the Warburg impedance has equal capacitative and resistive impedances, this is therefore also the resistance of the resistive part of the Warburg impedance. Therefore, when it is subtracted from R_r it gives what we have called θ.

Now Randles' k is related to his choice of a potential scale so that in his system the exchange current $\vec{i}$ at equilibrium is given by the relation

$$\vec{i}_{eq} = n\mathbf{F}ACk$$

where C is the concentration of the reactant to which k refers and A is the area of the interface. Substituting this into equation [26] gives Randles' equation. It may be mentioned that Gerischer (8) also derives an identical result. All four derivations are essentially the same, differing only in the number and character of the assumptions which give the appearance of entering into the result.

If $\alpha = \frac{1}{2}$, as is rather often the case, then from equation [25] and without assuming a state of equilibrium

$$RT/n\mathbf{F}\theta = i_{av} \qquad [27]$$

where i_{av} is the average of the absolute values of $\vec{i}$ and $\overleftarrow{i}$. In any case, whether $\alpha = \frac{1}{2}$ or not, the quantity defined by $RT/n\mathbf{F}\theta$ is an average of the absolute values of $\vec{i}$ and $\overleftarrow{i}$, weighted according to the fraction of the potential drop across the interface effective in promoting the forward reaction or hindering the reverse reaction. That is

$$i_{av} = \alpha\vec{i} + (1 - \alpha)\overleftarrow{i} \qquad [27a]$$

and with this definition, equation [27] is as valid as are equations [22] and [23].

It is assumed throughout the paper that only one faradaic process is taking place. If two faradaic processes take place simultaneously, it will usually be possible to consider each process independently and to regard each process as contributing an admittance in parallel with the double layer. This is permissible if the concentration changes produced by one faradaic process do not influence the second faradaic process. To show that this is so, one writes two equations like equation [15], one for each component of the faradaic current, but omitting from the equation for the first current the substances participating in the second reaction. The remainder of the derivation proceeds as before.

III. Classification of Substances

The substances present in the system are to be classified according to the kind of equivalent circuit which must be used to represent them. For substances which are formed or used up at the electrode, some kind of differential equation must usually be set up and solved, and such substances are naturally classified according to the kind of differential equation involved. However there are two kinds of substances which make virtually no contribution to the equivalent cir-

unit, and these are lumped together in class I. The scheme of classification follows:

Class I.—Substances for which $(\partial E/\partial v_o)dv_o/dt = 0$ or so nearly as to make no difference in the observable results. This class includes, first of all, those substances which do not participate in the electrochemical reaction. The factor $\partial E/\partial v_o$ is small because the concentration of a nonparticipating substance affects the activities of the participating substances only as a second order effect, say through its effect upon their activity coefficients. In addition, the factor dv_o/dt is small for nonparticipating substances. It is not zero because of the effect mentioned above whereby changes of concentration are sometimes produced incidental to the charging and discharging of the electrical double layer. This is in itself a small effect, and the product of two such small factors may be ignored safely.

It might be thought that the charging and discharging of the double layer would have a profound influence upon the faradaic current because of a "blocking" effect of the inert ions there. Upon closer examination this is found to be not so. Although it is true that a reducible ion, say cadmium, in the presence of an excess of an inert electrolyte, say potassium chloride, will be removed from the electrical double layer at sufficiently cathodic potentials, more will diffuse into the double layer at a rate controlled by the diffusion coefficient. Nothing is known of diffusion coefficients within the electrical double layer, but since it is the diffusion of a neutral substance (say cadmium chloride) which is under consideration, and since the thickness of the double layer is small compared to the thickness of the diffusion layer, there is no reason to suppose that changes in the concentration of the ions in the double layer will markedly affect the diffusion of cadmium chloride into it. That is to say, the normal mode of treatment of the diffusion of cadmium chloride will not be rendered invalid by the influence of the electrical double layer.

There is a further fact which tends to make this conclusion unsatisfactory. If substances of class I are present alone, there is no faradaic current and no faradaic admittance. Otherwise stated, θ is infinite for all possible reactions and the magnitude of the other impedances in series with it is inconsequential. If substances of class I are not present alone, then the substances of the other classes will have so large an effect upon the impedance, and especially upon the frequency dependence of that impedance, that their effects will entirely overshadow the trifling effects of substances of class I. Thus it does not appear to be necessary to consider in more detail an effect which can hardly make itself felt under any circumstances.

Another group of substances which is to be regarded as belonging to class I comprises those substances which participate in the electrochemical reaction but whose concentrations (or more strictly whose activities) do not change as a result of that reaction. Silver chloride at a silver surface in a solution of potassium chloride might constitute an example of such a substance. The activity of the silver chloride is invariant, or at least it is usual to regard it as such, making the factor dv_o/dt equal to zero. Possibly a newly formed deposit of silver chloride is not in its most stable state, so that it is not certain that this constitutes a bona fide example of a substance of class I. An even more doubtful example of such a substance is that of a solid metal which participates in the chemical reaction. Thus a newly formed deposit of metallic silver is quite likely to be in a state more chemically active than its standard state, in which case it would not be proper to regard dv_o/dt as identically zero. It should be mentioned in passing that for solids which change their chemical potential under strain it is necessary to regard v_o as the *activity* of the substance in question rather than its concentration. This follows from the fact that equation [15] and those which follow from it would not otherwise be significant, since the concentration is practically invariant whereas the chemical potential is not. For other substances it is much more convenient to retain the definition of v, w, etc., as concentrations.

Solvent molecules, even when they participate in the electrochemical reaction,[9] will ordinarily belong to class I.

Class II.—Substances which undergo periodic changes of concentration at the interface as a result of the electrochemical reaction, but which do not undergo secondary chemical reactions either before or after the electrochemical reaction. Such a substance might be a cadmium salt or other metallic salt with a reducible cation. The basic requirement to be met is that the concentration of the substance must be given at any instant by the diffusion laws together with Faraday's laws, and without the necessity of considering any further chemical reactions. In a solution of hydrochloric acid (with or without the admixture of other electrolytes) the substance HCl will belong to class II but hydrogen atoms will not (because they are subject to further reactions).

Class III.—Substances which undergo periodic changes of concentration at the interface as a result of electrochemical reaction, and which, in addition, combine with themselves spontaneously at the interface according to a second order rate law. It is further required that substances of this class shall not diffuse appreciably into either phase. This classification is intended to apply to hydrogen atoms on the surface of a metal into which they do not diffuse appreciably.

Class IV.—Substances which undergo periodic changes of concentration at the interface as a result of electrochemical reaction, and which are capable of diffusing into at least one phase, there to combine spontaneously according to a second order rate law. There is no need to consider a surface recombination here because the atoms are considered to be dissolved in the lattice and all concentrations are to be expressed in amounts per unit of volume. This contrasts with substances of class II where the unit of concentration is amount per unit of area. Class IV is primarily intended to represent hydrogen atoms on a surface which allows them to diffuse into it appreciably.

Class V.—In case a slow homogeneous chemical reaction precedes the electrochemical reaction, with only the product of the reaction directly involved in the electrochemical reaction, one has what Gerischer and Vetter have called a "vorgelagerten" reaction (8, 10). The substance immediately involved in the electrochemical reaction will then be said to belong to class V, whereas the substance which gives rise to it will belong to class I (supposing that it itself does not react at the electrode directly).

Class VI.—This class comprises substances such as metallic oxides and metallic films which are present in too small quantities to have the chemical and thermodynamic properties of the same substance in bulk. Thus a surface layer containing anywhere from a fraction of a monolayer to several molecular layers would belong to class VI. Such substances do not belong to class I because dw_o/dt does not vanish when the layer is so thin that it does not have its bulk value of chemical potential. On the other hand, some substances which would belong to class VI according to the definition just given must in fact be excluded from it. These are substances which are formed essentially instantaneously at the interface, so fast that there is no time lag (in the units of time which are experimentally significant) between their arrival at the interface and their reaction to form an adsorbed layer. For these substances equation [15a] does not apply; the current is a function not only of the variables listed, but also of dE/dt. Such substances are components of the electrical double layer and the current which goes to form it is not a faradaic current in the sense of our definitions. Thus iodide ions are adsorbed, we say, instantaneously, and if the potential is such that the compound of iodide ion and metal is not thermodynamically stable as a bulk sub-

[9] The term "electrochemical reaction" is here used in its original sense to mean any chemical reaction involving a transfer of charge from a metallic to an ionic conductor.

stance, the adsorbed ions remain at the interface, precluding the flow of more current to form more of the "compound." This happens, not because of geometric considerations, but because the adsorbed ions constitute part of the electrical double layer and generate an electric field which opposes the approach of more ions. If the bulk compound can form, that means that the opposing field is never large enough to prevent the approach and reaction of more ions. Then the current is faradaic.

In the case of very fast but not instantaneous reactions, the distinction between a faradaic and nonfaradaic current becomes somewhat arbitrary. Analytically the current is always faradaic if the reaction is not instantaneous, but if the reciprocal of the frequency is small compared to the half-time of reaction, the current can equally well be regarded as nonfaradaic. This is a small but intricate point which we shall not further consider here.

Further classes.—A class of substances could be defined to comprise those which form as a result of the electrochemical reaction, then diffuse into one or the other of the phases, there to react with one another according to a second order rate law. No substances are at present thought to belong to this class. Until some possible examples are uncovered, the class will not be given a number.

IV. The Differential Equations and Their Solutions

Substances of Class I

It has already been explained that substances in class I make no contribution to the faradaic admittance. This usually includes all but two substances, the oxidized and the reduced forms of what is commonly called the potential-determining substance.

Substances of Class II

This is the class of substances first treated by Warburg (2) and subsequently in various ways by many authors. The treatment to be given here has certain elements of novelty, particularly as regards the influence of transference, but is presented chiefly for the sake of clarifying what has long been considered a rather troublesome derivation. The troubles, it may be pointed out, have largely arisen from too little discussion of the many factors which need to be considered in order to justify the derivation.

The basic differential equation governing the diffusion of substances which do not undergo secondary chemical reactions is Fick's second law[10]

$$\partial w/\partial t = \epsilon \partial^2 w/\partial x^2 \qquad [28]$$

where w is the concentration of a substance W of this class and ϵ is the diffusion coefficient of the substance in whichever phase is under consideration. It need not be a constant as far as our conclusions are concerned because we shall be interested only in small (and in the limit zero) changes of concentration. A point which has escaped mention in previous treatments of this problem (but one which does not enter into the treatments of Randles or of Gerischer because they have limited their discussions in a way which eliminates this question) is that one cannot apply equation [28] to charged species except under rather special circumstances, namely in the presence of an excess of an inert electrolyte. Ions do not diffuse independently of one another except under these conditions, and it is necessary under other circumstances to choose for the substances in equation [15a] neutral substances and pairs of ions (i.e., salts) representing the electrolytes present. The faradaic current causes the appearance or disappearance at the interface of equivalent amounts of ion pairs, if one chooses to look at it this way, just as Faraday's laws can be expressed without reference to ions. If the faradaic current[11] is given as before by i, then the amount of the component W produced at the interface will be $i(\mu_c + t_c)$ or $i(\mu_a - t_a)$, with the understanding that if the anion and cation of the electrolyte are not present in equivalent concentrations, the one with the lesser concentration will be employed (because part of the other ion "belongs" to another salt). Here t_c and t_a are the fractions of the current carried by the cation or anion respectively of the ion pair W. μ_c is the "electrode transference number," the number of equivalents of the cation of the electrolyte W *produced* by the passage of one faraday of electricity across the interface. Ordinarily it will equal $+1$, -1, or 0 depending upon whether the cation is produced, used up, or neither. μ_a has the same significance for anions. We shall let $\mathcal{G}$ be the number of equivalents of the substance W *caused to appear* at the interface by the action of one Faraday of electricity[12] so that

$$\mathcal{G} = \mu_c + t_c \qquad \text{or} \qquad \mathcal{G} = \mu_a - t_a$$

according to which ion is present in the lower equivalent concentration. If the two are present at the same equivalent concentration, the two expressions are equal. In case W is a nonelectrolyte (not a salt) $\mathcal{G}$ will be positive or negative depending upon whether it is produced or consumed as a result of the electrochemical reaction.

This rather complicated system of nomenclature is necessitated by the fact that since ions do not diffuse independently of one another, one must treat the diffusion of salts rather than of ions. In order to understand how this has been done it is necessary to remember that transference does not by itself produce concentration changes. It does, however, affect the amount of uncharged electrolyte produced at the interface by the action of the current. This is the quantity which the factor $\mathcal{G}$ is intended to take into account.

If the faradaic current is given as before by $i_o + a \sin \omega t$, then the amount of component W caused to appear at the interface will be $\mathcal{G}$ times this, and all of this must be removed from the interface by diffusion or convection. The effects of convection will be neglected because the significant part of the present treatment has to do only with the alternating component of the current and hence only with the alternating component of the convection, which is surely negligible if not identically zero. Even if the solution is stirred, the effect of convection on the alternating component of the concentration will remain negligible, since any influence of stirring would be in the direction of rendering the effect smaller.

From Fick's first law of diffusion one would ordinarily write

$$-\epsilon \partial w/\partial x = i_o v_w + a v_w \sin \omega t \quad \text{at } x = 0 \qquad [29]$$

[10] The equations in this section refer always to a planar interface. However, if the radius of curvature is large compared to the half-thickness of the diffusion layer, the equations can be used also on curved surfaces. This point is discussed in somewhat more detail by Gerischer (8).

[11] If i is given in amp/cm², w will be expressed in coulombs/cm³ and ϵ in cm²/sec. In this system of units the area and Faraday's constant do not appear explicitly.

[12] The positive direction of the current will be assumed to be that for which electrochemical reduction occurs. $\mathcal{G}$ differs from μ because transference carries the ions of the substance W toward or away from the interface. Nevertheless one can speak of the number of moles of the neutral substance W *caused to appear* at the interface, because of the requirements of electroneutrality. One must distinguish between the meanings of the words "produced" and "caused to appear" in order to understand this point.

where ν_w is equal to $+\mathfrak{S}$ when diffusion occurs in the phase for which x is positive and to $-\mathfrak{S}$ when it occurs in the other. There is a fallacy in equation [29], however, in that it ignores the concentration changes produced by the nonfaradaic current. These are taken into account by writing instead of equation [29]

$$-\epsilon\partial w/\partial x = i_o\nu_w + a\nu_w \sin \omega t + b(t_c - \tau_c) \sin (\omega t + \delta) \quad \text{at } x = 0 \quad [30]$$

where δ is the phase angle between the faradaic and nonfaradaic currents, as before, and τ_c is the transference number of the electrical double layer for the cations. By this we mean the fraction of the current carried into or out of the electrical double layer by the cation in question, a quantity which can be and has been evaluated for the mercury-solution interface in a number of cases. It is equal to C^+/C, where C is the differential capacity of the electrical double layer and C^+ is the part of that capacity attributable to the entry and departure of cations during an infinitesimal transfer of charge. As before, if the concentration of cations in the solution is not equivalent to or less than that of the anion with which it is considered to be associated, then one should write $\tau_a - t_a$ for $t_c - \tau_c$.

To begin with we shall consider that the final term in equation [30] can be neglected, making equation [29] valid. This will be so in the presence of an excess of an inert electrolyte (then t_c and τ_c will both be essentially zero) or in case the ratio b/a is small (in the presence of considerable faradaic current) or in case $t_c = \tau_c$, which can easily happen because τ_c varies with the potential.

A further condition which must be satisfied is that $w \to$ constant as $|x| \to \infty$. In order to solve equation [29] completely it would be necessary to impose some further boundary conditions as well. Thus one could require that $w = 0$ for all values of x when $t = 0$, or any other condition representing a desired initial condition. In any case the solution takes the form

$$w = f(x, t) + (a\nu_w\lambda\epsilon^{-x/\lambda}/2\epsilon)\left[\sin\left(\omega t - \frac{x}{\lambda}\right) - \cos\left(\omega t - \frac{x}{\lambda}\right)\right] \quad [31]$$

where

$$\lambda = (2\epsilon/\omega)^{\frac{1}{2}} \quad [32]$$

and $f(x, t)$ is a function of x and t satisfying equations [28] and [29] when $a = 0$, i.e., when there is no superimposed alternating current. If W is a product of the electrochemical reaction, and in the absence of further boundary conditions, w will increase without limit at all values of x as t increases. This is physically evident (since there is no mechanism for removing W from the system) but will not be proved since it is not essential to the argument. It is of considerable practical importance, however, since it means that no steady state can be reached by diffusion alone. Thus in ordinary polarographic measurements it is necessary to achieve a reproducible state which is not a steady state by continually replacing the electrode. If a solid electrode which cannot readily be replaced is used, provision must be made for removing the products of electrolysis or no steady state can be achieved. Thus in any discussion of the properties of electrodes one must consider either a steady state or a reproducible state based upon some known conditions at a particular value of t. If a steady state is under consideration, $f(x, t)$ will reduce to a function of x alone, in which case it will contribute nothing to $\partial w/\partial t$ and therefore contributes nothing to the remainder of the discussion and could as well be dropped.

When a reproducible but not steady state is considered, the situation is not quite so simple. Then w will be a slowly varying function of time, and it is necessary to consider whether a Fourier analysis of this function would yield a component of frequency $\omega/2\pi$. This is a fairly complex problem to which only a practical answer will be given. If the repetition rate of the phenomenon (the reciprocal of the drop time for instance) is small compared to the frequency under investigation, only a small contribution to $\partial w/\partial t$ will arise in this manner. Then it will be possible to detect the contribution of the superimposed current in spite of a background of "noise" arising from the lack of a steady state. The unwanted contribution to $\partial w/\partial t$ will be incoherent (of random relative phase) and will therefore contribute no systematic error to the observation of $\partial w/\partial t$. This means that for our purposes we can ignore $f(x, t)$ in equation [31] even when a true steady state has not been achieved.

From equation [31]

$$\partial w_o/\partial t = (a\nu_w\sqrt{\omega/2\epsilon})(\sin \omega t + \cos \omega t) \quad [33]$$

where it will be recalled that w_o is w at $x = 0$. This result can be inserted into equation [19] to give

$$a\omega R_s \cos \omega t + (a/C_s) \sin \omega t = \theta a\omega \cos \omega t + \gamma\, dv_o/dt + (\beta a\nu_w\sqrt{\omega/2\epsilon})(\sin \omega t + \cos \omega t) + \cdots \quad [34]$$

So far it has been considered that W is a substance capable of diffusing only in one phase. It might conceivably be able to diffuse into both phases, or one might have two substances of class II, one of which diffuses into one phase and the other into the other. In any case the equations are to be set up anew for each phase and for each substance. The solutions are independent of one another. Thus for two substances of class II, two sets of differential equations would be set up and solved (independently) and the appropriate values of $\partial w_o/\partial t$ employed in equation [19]. The second substance could be called V in equation [19], but this will not be done because we wish to reserve the symbol V for substances of classes III and IV. Instead we shall use the subscripts $_1$ and $_2$ to denote two substances of the same class (or a single substance capable of diffusing in both phases) and their associated properties. Then for each substance in each phase where it occurs, a result having the form of equation [33] will be found and equation [34] will become

$$\begin{aligned} a\omega R_s \cos \omega t + (a/C_s) \sin \omega t &= \theta a\omega \cos \omega t \\ &+ (\beta_1 a\nu_{w_1}\sqrt{\omega/2\epsilon_1})(\sin \omega t + \cos \omega t) \\ &+ (\beta_2 a\nu_{w_2}\sqrt{\omega/2\epsilon_2})(\sin \omega t + \cos \omega t) \\ &+ \cdots + \gamma\, dv_o/dt + \cdots \end{aligned} \quad [35]$$

which may be written for short

$$a\omega R_s \cos \omega t + (a/C_s) \sin \omega t = \theta a\omega \cos \omega t + a\eta\omega^{\frac{1}{2}}[\sin \omega t + \cos \omega t] + \gamma\, dv_o/dt + \cdots \quad [36]$$

where

$$\eta = \sum_i \beta_i\nu_i/(2\epsilon_i)^{\frac{1}{2}}. \quad [37]$$

In case all the substances present are of classes I and II the final term in equation [36] can be dropped. Equating coefficients of $\sin \omega t$ and of $\cos \omega t$ gives the two equations:

$$R_s = \theta + \eta/\omega^{\frac{1}{2}} \quad [38]$$

$$C_s = 1/\eta\omega^{\frac{1}{2}} \quad [39]$$

or after eliminating η

$$R_sC_s\omega = 1 + \theta C_s\omega. \quad [40]$$

When the reaction in question is infinitely fast (in the absence of diffusion control), $\theta = 0$. This is apparent from the definition of θ, equation [17], or from equation [27]. In that case

$$R_s C_s \omega = 1 \qquad [41]$$

which was Warburg's result (2). It is now seen that that equation is expected to be valid only after correcting for the capacity of the electrical double layer [as was first pointed out by Krüger (3)] and with the added restriction that the electrochemical reaction be infinitely fast in the absence of diffusion control. In addition it is necessary that all of the substances present belong to classes I or II.[13]

It is possible and helpful to visualize equations [38] to [41] with the aid of a simple device. We note first that $R_s C_s \omega = \cot \Omega$, where Ω is the phase angle between the current and impedance vectors of a circuit consisting of a resistor R_s and a condenser C_s in series. Then a circuit for which $R_s C_s \omega = 1$ at all frequencies would be one for which $\Omega = \pi/4$ at all frequencies. The resistive and capacitative components of the impedance therefore remain equal. Moreover the resistance and capacity both vary inversely as the square root of the frequency (cf. equations [38] and [39]). Expressed as a parallel circuit, the resistance and capacity would again vary inversely as the square root of the frequency, although the resistance would be twice as great and the capacity half as great as before. All of these properties may be included in a new symbol:

which will be termed a Warburg impedance in recognition of the fact that Warburg seems to have been the first to describe its properties and to relate them to this problem (2). The important thing to note about the Warburg impedance is that it is not the same as any combination of fixed capacitors and resistors because its change of impedance with frequency is different from any of these. At zero frequency its impedance becomes infinite in magnitude, but it is important not to confuse zero frequency with direct current in this circuit, since its resistance to direct current is not infinite but finite and indeterminate (by definition). In this respect, also, it is unlike the series or parallel combination of any ordinary impedances. The reason for setting its d-c resistance equal to an indeterminate but finite value is that the differential equation whose solution it is intended to represent does not demand an infinite resistance to direct current but rather the reverse, i.e., a finite resistance to permit the passage of the faradaic current. The resistance is indeterminate because it depends upon the function $f(x, t)$ whose form depends upon unspecified boundary conditions.

To make the Warburg impedance quantitative it will be said to have the magnitude η when its impedance satisfies equations [38] and [39] (*with* $\theta = 0$). When the only substances in the system are those of classes I and II, when the interface is smooth and homogeneous, and when the last term in equation [30] is zero, the entire system, metal-solution, can therefore be represented by the equivalent circuit shown in Fig. 1, where C_{dl} is the double layer capacity, R_{soln} is the resistance of the solution, θ is a pure resistance equal to $RT/n\mathbf{F}i_{av}$, and-W- is the Warburg impedance defined

[13] These conclusions are implicit in the writings of all recent authors. A discussion of the diffusion wave is given by Gerischer (8).

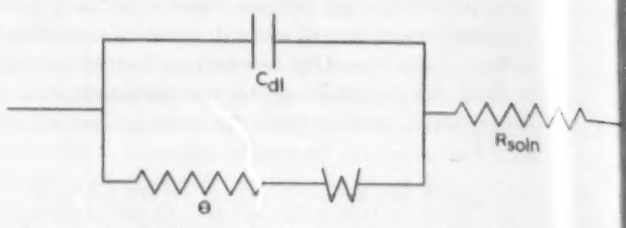

FIG. 1. Equivalent circuit for the system containing substances of classes I and II.

above. This statement summarizes the results obtained up to this point.

It is easy to evaluate β_i in case the diffusing substance W_i is present at low enough concentrations so that the rate of change of its activity coefficient with concentration is small, provided the net current is zero, and provided the substance is what is ordinarily called the potential-determining substance (or one state of the potential-determining substance) in that phase. Then the Nernst equation is valid (because the system is at equilibrium) and we may write from the definition of β (equation [17])[14]

$$(\beta_i)_{eq} = -RT/n_i\mathbf{F}w_i \qquad [42]$$

where w_i is the concentration of W_i close to the interface but not in the electrical double layer itself. The reason for restricting the definition of w_i to a position just outside the double layer is that the Nernst equation refers to the composition of the bulk solution with which the interface is in equilibrium.

The Warburg impedance is now fully defined for the equilibrium case in terms of ordinary variables. Equation [37], when used in conjunction with equation [42], gives a result in agreement with, but somewhat more general than, Randles' equations [16] and [17]. Gerischer (8) gives a similar result (referred to the diffusion of a single substance in a single phase), and so does Ershler (7).

It is of interest that $(\beta_i)_{eq}$ is not a function of the specific reaction rate constant, and the same is therefore true of η. This is in agreement with the observation of Randles (6) that surface-active materials reduce the exchange current but do not affect the Warburg impedance at equilibrium.

The constant β_i can be evaluated for nonequilibrium conditions through the use of equations [22], [23a], and [27] as follows:

$$\beta_1 = \left(\frac{\partial E}{\partial w_1}\right)_i = -\left(\frac{\partial E}{\partial i}\right)_{w_1}\left(\frac{\partial i}{\partial w_1}\right)_E = -\theta\left(\frac{\partial i}{\partial w_1}\right)_E \qquad [42a]$$

$$= -\theta\vec{i}/w_1 = -(RT/n\mathbf{F}w_1)(\vec{i}/i_{av}). \qquad [43]$$

Likewise $$\beta_2 = \theta\vec{i}/w_2 = (RT/n\mathbf{F}w_2)(\vec{i}/i_{av}) \qquad [44]$$

where i_{av} is the weighted average defined by equation [27a].

Equations [43] and [44] elucidate the behavior of the pseudocapacity as one goes through the half-wave potential in a typical polarographic experiment with a reversibly reducible ion such as Cd^{++}. At all potentials $\vec{i}/i_{av}$ is of the order of magnitude unity (it lies between unity and $1/\alpha$ because the reverse current never exceeds the forward current) and there-

[14] This use of the Nernst equation does not introduce the assumption that equilibrium persists during the changes of composition caused by the passage of the alternating current. What is done is to evaluate β from its definition. In this connection note that equation [43], which is obtained without the use of the Nernst equation, could also be used to derive equation [42].

fore β_1 depends chiefly upon w_1. This means that β_1 will be very large at potentials considerably above the half-wave potential, but not elsewhere.

In a similar way $\vec{i}/i_{av}$ will be of the order of magnitude unity or less (because $\overleftarrow{i}/i_{av} = \vec{i}/i_{av} - i/i_{av}$), so that large values of β_2 can be realized only when w_2 is very small This happens below the half-wave potential. Now η depends upon the *sum* of $|\beta_1|$ and β_2 (or more strictly of $|\beta_1|/\sqrt{\epsilon_1}$ and $\beta_2/\sqrt{\epsilon_2}$, see equation [37]), and since β_1 is large above the half-wave potential and β_2 is large below it, and since neither is large in the neighborhood of it, it follows that η will reach a minimum in the neighborhood of the half-wave potential (for reversibly reducible ions). A large value of η means a small faradaic admittance, which is to say that the pseudocapacity and polarization resistance associated with the reversible reduction and oxidation of the ion will disappear at potentials somewhat removed from the half-wave potential.

As one would expect from common sense considerations, the faradaic admittance is very small below the half-wave potential for another reason, namely that there is practically no faradaic current. In terms of the present formulation of the theory, θ becomes large below the half-wave potential because i_{av} is very small there (cf. equation [26]). A large value of θ restricts the faradaic admittance for the same reason that a large value of η does.

The situation is considerably different from that discussed above when we come to consider reactions which are not reversible. In terms of the present nomenclature, these are reactions for which the exchange current is small at the equilibrium potential. Then θ is large at that potential and the faradaic admittance will not appear. The half-wave potential (where $i = i_d/2$) will be somewhat greater than the equilibrium potential in this case. There θ will be smaller than at the equilibrium potential (because i_{av} is now much larger) but is not necessarily small enough to permit the observation of the faradaic admittance. In order to discuss this case satisfactorily it is necessary to put it into mathematical form.

This can be done by considering an idealized arrangement patterned after the polarograph but much simpler to analyze mathematically. Such an arrangement, which we shall call a superpolarograph, can be imagined as follows: mercury and the solution under investigation (containing a reducible substance in small amounts and an inert electrolyte in much larger amounts) will be supposed to be in contact at a plane interface. At some arbitrarily chosen plane lying parallel to the interface and within the solution the reducible substance W_1 will be supposed to be added to the system at a rate equal to that at which it is being removed from the system by the action of the electric current. Under steady-state conditions the concentration of W_1 will be a linear function of the distance between the interface and the plane selected above. Its concentration at the interface, w_1, will be a linear function of the current so that

$$w_1 = w_1^o(1 - i/i_d) \qquad [44a]$$

where w_1^o is the concentration in the interior of the solution and i_d is the diffusion current, i.e., the current which flows when the potential is such that only the rate of diffusion limits the current.

In a similar way the product of the reduction, W_2, will be supposed to be removed (by unspecified means) from an arbitrarily selected plane lying parallel to the interface within the phase into which W_2 diffuses. Its concentration gradients will again be linear and the equation for w_2, the concentration at the interface, will be

$$w_2 = w_2^o(i/i_d) \qquad [44b]$$

where w_2^o is the upper limit of concentration of W_2 at the interface when the diffusion current i_d is flowing steadily.

These equations are probably approximately valid under *ordinary* polarographic conditions, for which the exact equations are not known.

The remainder of the calculation is purely algebraic. Equations [44a] and [44b] are first substituted into equations [22]

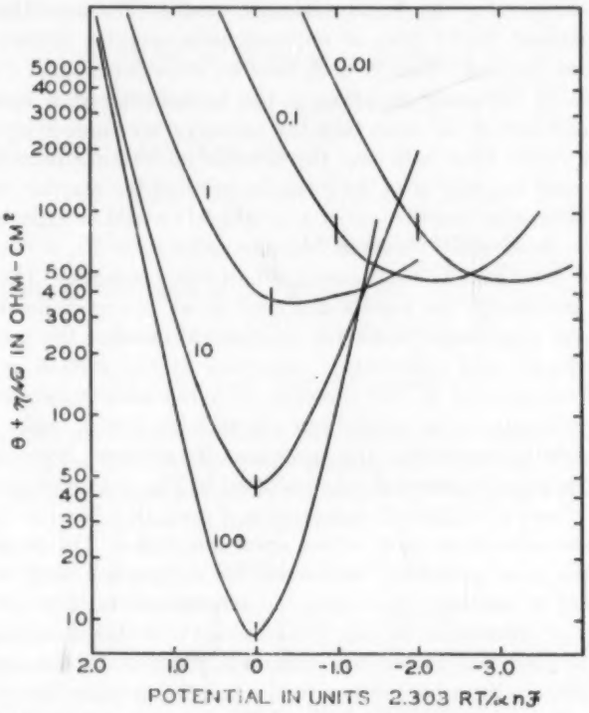

FIG. 2. Faradaic impedance, $\theta + \eta/\sqrt{\omega}$, vs. potential measured in units of $2.303RT/\alpha n\mathbf{F}$. Zero potential is equilibrium potential. Short vertical lines represent half-wave potentials. Constants used were as follows: $T = 298°$; $n = 2$; $\alpha = \frac{1}{2}$; $i_d = RT/200n\mathbf{F} = 1.48 \times 10^{-4}$ amp/cm²; $w_1^0\sqrt{\omega\epsilon_1} = RT/n\mathbf{F} = 0.0295$ amp/cm²; $w_1^0\sqrt{\epsilon_1}/w_2^0\sqrt{\epsilon_2} = 1$; $n\mathbf{F}w_1^0k_1 = 100$, 10, 1.0, 0.1, or 0.01 amp/cm² as marked on curves.

and [23] and the resulting equations solved, together with equation [23a], for $\vec{i}$ and $\overleftarrow{i}$. The results are

$$\vec{i} = \frac{f}{1 + f - fh/(1 + h)}\, i_d \qquad [44c]$$

$$\overleftarrow{i} = \frac{fh}{(1 + h)(1 + h - fh/[1 + h])}\, i_d = \frac{\vec{i}}{1 + h}\, h \qquad [44d]$$

where $f = [n\mathbf{F}w_1^o k_1 \exp(\alpha n\mathbf{F}E/RT)]/i_d$ and

$$h = [n\mathbf{F}w_2^o k_2 \exp\{-(1 - \alpha)n\mathbf{F}E/RT\}]/i_d.$$

With these values of $\vec{i}$ and $\overleftarrow{i}$ it is a simple matter to find w_1 and w_2 (from equations [44a] and [44b]) and so to evaluate β_1 and β_2. The results are

$$-\beta_1 = \frac{RT}{n\mathbf{F}w_1^o}\,\frac{1 + f + h}{\alpha + h} \qquad [44e]$$

$$\beta_2 = \frac{RT}{n\mathbf{F}w_2^o}\,\frac{h}{f}\,\frac{1 + f + h}{\alpha + h} = -\beta_1\,\frac{w_1^o i_d}{w_2^o f}. \qquad [44f]$$

With suitable values of the constants, this is all one needs for the evaluation of the faradaic impedance (equations [37–39]). A plot of the logarithm of $\theta + \eta/\omega^{\frac{1}{2}}$ is given in Fig. 2

for a suitable choice of constants and for various values of $n\mathbf{F}w_1{}^\circ k_1$, which has to do with the intrinsic speed of the reaction. The curve with the lowest minimum corresponds to a fast reaction and the remaining curves in the numbered order correspond to successive ten-fold decreases in the intrinsic speed, $n\mathbf{F}w_1{}^\circ k_1$. The half-wave potential is marked with a short vertical crossline on each curve. The ratio of k_1 to k_2 is kept constant, which means that the equilibrium potential is kept constant and may be considered to be at $E = 0$.

It will be seen from the curves that the half-wave potential shifts in the direction of more cathodic potentials as the intrinsic speed of the reaction is made smaller. The same thing is without doubt true of ordinary polarographic measurements. The minimum in each faradaic impedance curve also shifts in the same direction as the intrinsic speed is made smaller and at the same time the minimum increases in absolute value. That is to say, the faradaic admittance becomes less easy to observe as the intrinsic speed of the reaction becomes smaller and the potential at which it would be expected to be most easily observed becomes more cathodic, shifting even more rapidly than does the half-wave potential. These are essentially the results observed in an ordinary polarographic experiment when one attempts to measure the pseudocapacity and polarization resistance at the surface of a mercury droplet in the presence of a reducible substance. Experiments so far carried out are still too few to make it possible to assert that the agreement is complete, however.

The actual numerical values plotted in Fig. 2 depend upon the choice of numerical constants and even the shape of the curves depends to some extent upon this choice. The values chosen were considered reasonable for comparison with the results of ordinary polarographic measurements. For purposes of orientation, it may be mentioned that the impedance of the electrical double layer amounts to about 10 ohm-cm^2 at 1000 cycles, which shows that a parallel faradaic impedance of several hundred ohms might be expected to be difficult to measure. That is why the pseudocapacity and polarization resistance seem to come in only over a very limited range of potentials, as observed.

The more general boundary condition, equation [30], will now be considered. The solution is the same as that already found except that it now contains an additional term[15] w', having the same form as the first. Then

$$w = \text{right side of equation [31]} + w'$$

$$w' = \{b(t_c - \tau_c)\lambda e^{-x/\lambda}/2\epsilon\} \cdot \left\{\sin\left(\omega t + \delta - \frac{x}{\lambda}\right) - \cos\left(\omega t + \delta - \frac{x}{\lambda}\right)\right\} \quad [45]$$

and

$$\partial w_o'/\partial t = \{b(t_c - \tau_c)/\lambda\}\ \{\cos(\omega t + \delta) + \sin(\omega t + \delta)\} \quad [46]$$

where w_o' is w' at $x = 0$. Expanding the sine and cosine terms, substituting the result into equation [19], and equating coefficients of the terms in sin ωt and in cos ωt gives

$$R_s{}^{II'} = [q(t_c - \tau_c)/(2\epsilon\omega)^{\frac{1}{2}}][\cos\delta + \sin\delta] \quad [47]$$

$$1/C_s{}^{II'} = [q(t_c - \tau_c)/(2\epsilon\omega)^{\frac{1}{2}}][\cos\delta - \sin\delta] \quad [48]$$

where q (equals b/a) is given by equation [12], δ by equation [11], and where $R_s{}^{II'}$ is the equivalent series resistance of that part of the faradaic admittance attributable to the effect upon the faradaic admittance of the concentration changes caused by the nonfaradaic current. $C_s{}^{II'}$ has a similar meaning relating to the capacity.

The impedance defined by equations [47] and [48] will be called $Z^{II'}$ and could be represented by the symbol -II'-, a kind of an extra Warburg impedance. Strictly speaking $Z^{II'}$ and -II'- will refer to a summation of terms of the form of equations [47] and [48], one for each substance of class II in the system. Since both δ and q are in themselves functions of the frequency, it is understandable that the impedance -II'- will be a complicated function of the frequency. For this reason it is preferable where possible to make $t_c - \tau_c = 0$. This can be done most easily by having an excess of an inert electrolyte present.

Substances of Class III

Class III comprises substances which are formed at the interface but which are incapable of undergoing diffusion and which combine with themselves on the surface according to a second order rate law. The most obvious example of this is that furnished by atomic hydrogen on the surface of a metal into which it cannot diffuse. The initial product of the electrolysis (say, hydrogen atoms) reacts either with itself in a bimolecular reaction or electrochemically with another component of the solution (hydronium ions or water) to form hydrogen molecules. More generally, the initial product, V, reacts either chemically or electrochemically to produce a substance V_2 (a dimer of V). This reaction is to be considered spontaneous, so that $\Delta\mathbf{F} < 0$ and equilibrium does not exist between V and V_2. If equilibrium *does* exist, then V and V_2 are to be regarded as forms of the same substance. In other words, subsequent reaction of V to form V_2 does not then affect the results. If equilibrium exists, the reaction by which it is attained must be rapid relative to the slow step, as is evident kinetically. Thus one does not have to consider the case where equilibrium exists but is attained only slowly, that being a contradiction in terms as long as current is flowing.

Two kinds of secondary reaction need to be considered. It is of interest that the problem can be treated without assumptions as to the relative importance of the two. We shall begin by reviewing the nomenclature often used in discussion of this subject and explicitly set down by Parsons and Bockris (12) as follows:

1. The discharge reaction: "A proton is transferred from the solution side of the [interface] to an adsorption position on the electrode surface. The transfer is understood to involve the simultaneous neutralization and desolvation of the proton."

2. The catalytic reaction: "Two hydrogen atoms adsorbed on the electrode surface combine to form a hydrogen molecule."

3. The electrochemical reaction: "A proton is transferred from the solution side of the [interface] in such a way that it combines immediately with a hydrogen atom adsorbed on the electrode surface and with an electron from the metal."

As Parsons and Bockris point out; "It may be noted that the discharge reaction must occur during all cathodic evolution of hydrogen while the catalytic and electrochemical reactions are alternative (or simultaneous) processes." In the discussion to follow we shall consider them as simultaneous processes, this being the general case. No assumptions are needed concerning the rate-determining process.[16]

[15] This use of the prime is not related to the use made of it in equation [15].

[16] Strictly speaking there is no one "slow step" in the discharge of hydrogen ions under steady-state conditions, since

Although the system of nomenclature here described is rather often used (usually with unspecified variations) in the literature, it is the contention of the present writer that it is not etymologically satisfactory. Thus the reaction $H + H \rightarrow H_2$ is not a *catalytic* reaction, although it is probably a *catalyzed* reaction. A descriptive name which is noncommital as to mechanism is much to be preferred. With this in mind we shall call it the combination reaction.

The names "discharge reaction" and "electrochemical reaction" are likewise unsatisfactory in that either name could apply to either reaction. Both are electrochemical and both are discharge reactions. We shall call them by the descriptive names "primary discharge" and "secondary discharge" reactions. In general the distinction will be that the primary discharge reaction does not involve previous products of discharge, whereas the secondary discharge does.

The discharge of hydronium ions (or of water) therefore starts with the primary discharge reaction, producing hydrogen atoms. The recombination and secondary discharge reactions then compete for these hydrogen atoms. The differential equation to be satisfied by v_o, the concentration of hydrogen atoms on the surface, is:

$$dv_o/dt = m(i_o + a \sin \omega t) - (1 - m)(i_o + a \sin \omega t) - kv_o^2 \quad [49]$$

where m is the fraction of the current carried by the primary discharge reaction, and k is the reaction rate constant for the combination reaction, taken to be second order, as is extremely probable for a bimolecular reaction. It is not at all difficult to derive comparable equations for other orders, but this will not be done in the absence of any information suggesting that it may be physically important to do so.

Equation [49] is *stoichiometric* in character and asserts that the rate of increase of concentration of V equals the rate at which hydrogen atoms are added to the surface by the primary discharge reaction, minus the rate at which they are removed by the secondary discharge reaction, minus the rate at which they are removed by the combination reaction. It is interesting and important that it is not necessary to know the rate law for the secondary discharge reaction, since this would introduce a large element of uncertainty into the calculation if it were needed.

For convenience of notation let $g = 2m - 1$. Then g varies from unity (no contribution from the secondary discharge reaction) to zero (no contribution from the combination reaction). Equation [49] becomes

$$dv_o/dt = i_o g + ag \sin \omega t - kv_o^2. \quad [50]$$

This equation has been solved completely for an appropriate set of boundary conditions,[17] but since the complete solution is not needed, but only the steady-state solution, only the latter will be given here. It can be found very readily by noting that the steady-state solution must be of the form:

$$v_o = v_a + A \sin \omega t + B \cos \omega t \quad [51]$$

where v_a is the steady-state concentration of V, and A and B are small constants (approaching zero in the limit) to be evaluated. The necessity for the form of equation [51] arises from the fact that all harmonics will be infinitesimals of higher order than the first and can therefore be neglected, as is known in theory and as is also borne out by the complete solution mentioned above.

Substituting equation [51] into equation [50] and equating coefficients of like terms gives the three equations:

$$v_a = (i_o g/k)^{\frac{1}{2}} \quad [52]$$

$$A = agG/(G^2 + \omega^2) \quad [53]$$

$$B = -ag\omega/(G^2 + \omega^2) \quad [54]$$

where $G = 2(i_o g k)^{\frac{1}{2}} = 2v_a k$.

From equation [51] one can find dv_o/dt

$$dv_o/dt = A\omega \cos \omega t - B\omega \sin \omega t \quad [55]$$

which when substituted into equation [36] gives

$$a\omega R_s \cos \omega t + (a/C_s) \sin \omega t = \theta a\omega \cos \omega t + a\eta\sqrt{\omega}[\sin \omega t + \cos \omega t] + \gamma A\omega \cos \omega t - \gamma B\omega \sin \omega t. \quad [56]$$

Equating coefficients of like terms gives

$$R_s = \theta + \eta/\sqrt{\omega} + \gamma g G/(G^2 + \omega^2) \quad [57]$$

$$1/C_s = \eta\sqrt{\omega} + \gamma g \omega^2/(G^2 + \omega^2). \quad [58]$$

We now define an impedance -III- whose properties are those defined by the last terms of equations [57] and [58]. That is to say, the equivalent series resistance R_s^{III} and capacitance C_s^{III} will be given by the relations

$$R_s^{III} = GJ/(G^2 + \omega^2) \quad [59]$$

$$C_s^{III} = (G^2 + \omega^2)/\omega^2 J \quad [60]$$

and also $$R_s^{III} C_s^{III} \omega = G/\omega \quad [61]$$

where $J = \gamma g$, a constant.

This impedance can be more simply represented by means of its equivalent parallel circuit.[18] With the usual conversion formulas, namely

$$R_p = R_s(1 + \zeta^2)/\zeta^2$$

$$C_p = C_s/(1 + \zeta^2)$$

where $\zeta = R_s C_s \omega$

one has

$$R_p^{III} = J/G = \gamma\sqrt{g}/2\sqrt{i_o k} \quad [62]$$

$$C_p^{III} = 1/J = 1/\gamma g \quad [63]$$

where R_p^{III} and C_p^{III} are the equivalent parallel components.

The above treatment assumes that g does not vary as a result of the flow of alternating current. It is evident that this will be true when g is either close to unity or close to zero. It will be shown in a subsequent publication that g is ordinarily very close to unity.

It is now possible to depict an equivalent circuit covering systems of substances of classes I, II, and III. It should be recognized that there will always be a substance of class II present along with one of class III, so that the Warburg impedance is present in any case unless β (and therefore also η) is negligible. This can happen, however, as described just

all steps in series are necessarily equally fast. But there may be a rate-determining step in the sense that one step has a low rate constant whereas the others are held in check by extremely small concentrations of the reactants.

[17] The author is grateful to Professor R. Breusch of the Amherst College Department of Mathematics for assistance in obtaining this solution.

[18] The author is grateful to Dr. H. Gerischer for pointing out to him that this transformation results in a simplification of the result.

below, in which case the substance of class II might be said to have degenerated to class I.

Supposing for the moment that this has not happened, the equivalent circuit for a system containing substances of classes I, II, and III will be as represented in Fig. 3.

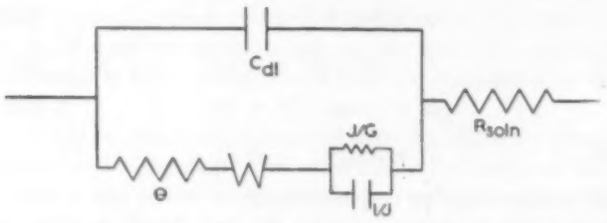

FIG. 3. Equivalent circuit for a system containing substances of classes I, II, and III.

It is to be anticipated that the Warburg impedance will be unobservable in neutral or alkaline aqueous solutions not containing any easily reducible substance. Then the only reducible substance is water (at potentials such that the cation present is not reduced), and this belongs to class I, making no contribution to the impedance. The hydroxyl ion, to be sure, belongs to class II and in principle gives rise to a Warburg impedance. As a practical matter it does not do so for the following reason: looking at equation [42a], β_1 is seen to be the product of two factors, θ and $(\partial i/\partial w_1)_E$. The latter is negligible if not identically zero because the rate of water reduction does not depend significantly upon the concentration of hydroxyl ion. This is true, at any rate, where the rate of the back reaction is small. Therefore β_1 will be small compared to θ, since $(\partial i/\partial w_1)_E$ is the ratio of the two. This means that the Warburg impedance will always be negligible compared to θ, so that regardless of its absolute magnitude, it will not be observed in neutral or alkaline solutions.

This argument applies to any case where the reverse current is small compared to the forward current *provided* the product of the forward reaction does not influence by its presence the rate of the forward reaction.

In the absence of a continuous direct faradaic current $i_o = 0$ and the resistance J/G becomes infinite, i.e., it disappears from the equivalent circuit. This makes the equivalent circuit so simple that it should be feasible to evaluate J and θ experimentally. All of this is predicated upon the possibility of obtaining a smooth homogeneous surface of a metal whose overvoltage is not so high as to make θ very large and the faradaic admittance correspondingly negligible (as is the case with mercury). Gallium would appear to be a suitable metal for this purpose.

At high frequencies the faradaic admittance always approaches θ, and unless this latter is zero the measured over-all series resistance and capacity will approach R_{soln} and C_{dl} respectively. This can be shown mathematically by deriving an equation for the over-all impedance, but it is easier to note that the limiting impedance will always be that of the circuit which carries the current at the limiting frequency. Thus as long as the faradaic impedance contains a finite resistance θ, its impedance cannot fall below that value. The nonfaradaic branch, on the other hand, is capacitative in character so that its impedance falls below any pre-established finite value as the frequency is increased indefinitely. This means in practice that it is the resistance of the solution and the capacity of the electrical double layer which are measured in the limit as the frequency is indefinitely increased. The accuracy of the measurements falls off with increasing frequency, however, particularly as regards the measurement of the series capacity, so that it is always necessary to use an appropriate extrapolation technique, making the best possible use of the data at intermediate frequencies.

Even if θ is zero, corresponding to an infinitely fast reaction, the measured impedance will still approach the same value at high frequencies. This follows from the fact that γ will not then be negligible, meaning that there will be a Warburg impedance. But the Warburg impedance falls off with increasing frequency more slowly than does a pure capacitance, which means that an ever-increasing fraction of the alternating current goes by way of the nonfaradaic (double layer) admittance, so that it is this which is measured in the limit.

In order to evaluate γ note first that

$$i = \vec{i_p} - \overleftarrow{i_p} + \vec{i_s} - \overleftarrow{i_s}$$

where the subscripts p and s refer to the primary and secondary discharge currents, respectively. Then

$$\partial i/\partial w_2 = \partial \vec{i_p}/\partial w_2 - \partial \overleftarrow{i_p}/\partial w_2 + \partial \vec{i_s}/\partial w_2 - \partial \overleftarrow{i_s}/\partial w_2 \quad [63a]$$

and just as before

$$\gamma = \partial E/\partial w_2 = \theta\, \partial i/\partial w_2. \quad [63b]$$

Of the four terms in $\partial i/\partial w_2$, only the second and third are different from zero (and the latter only if $g \neq 1$).

Substances of Class IV

Substances of class IV differ from those of class III in that they are by definition capable of diffusing into one of the two phases, or even into both. They differ from substances of class II in that they are able to combine with themselves in a second order reaction *at the interface*. Hydrogen atoms presumably belong to this class when the metal is one which permits the diffusion of hydrogen (in the form of atoms). An alternative situation in which the hydrogen atoms diffuse into the metal, *there* to combine to form molecular hydrogen, has also been worked out in full detail[19] but the solution will not be presented because it now appears unlikely that this situation ever arises either with hydrogen or with any other substance which might be thought to combine with itself in a second order reaction in the interior of one of the phases.

The basic differential equation to be solved is again equation [28], written now for a substance V

$$\partial v/\partial t = \epsilon \partial^2 v/\partial x^2 \quad [28]$$

subject to the condition

$$-\epsilon \partial v/\partial x = i_o g + ag \sin \omega t - kv^2 \text{ at } x = 0. \quad [64]$$

In addition one has naturally the condition that $v \to 0$ as $x \to \infty$. In these equations, ϵ is the diffusion coefficient of the substance V (hydrogen atoms) in the metallic lattice, and k is as before the reaction rate constant for the combination of hydrogen atoms to form hydrogen molecules at the surface. A steady-state solution to equation [28] which can be made to fit the boundary conditions by a suitable choice of constants is

$$v = v_o - \left(\frac{i_o g - k v_o^2}{\epsilon}\right) x + \frac{ag\lambda M \epsilon^{-x/\lambda}}{2\epsilon} \left[\sin\left(\omega t - \frac{x}{\lambda} + \varphi\right) - \cos\left(\omega t - \frac{x}{\lambda} + \varphi\right)\right] \quad [65]$$

[19] This was the first case of this type to be worked out by us. The author is indebted to Professor William T. Scott of the Smith College Department of Physics for providing us with the

where $\lambda = \sqrt{2\epsilon/\omega}$, v_o = the concentration of V at the interface in the absence of the alternating current, and M and φ are constants (independent of x and t but not of ω) to be determined by the boundary conditions. By differentiation and substitution they are found to be

$$\varphi = \arctan [s/(1 + s)] \quad [66]$$

$$M = 1/(1 + 2s + 2s^2)^{\frac{1}{2}} \quad [67]$$

where $$s = \lambda k v_o/\epsilon = k v_o(2/\omega\epsilon)^{\frac{1}{2}}. \quad [68]$$

Then from equation [65]

$$\partial v_o/\partial t = (gaM/\lambda)\{\cos(\omega t + \varphi) + \sin(\omega t + \varphi)\} \quad [69]$$

which gives, when substituted into equation [36], after equating coefficients of $\omega \cos \omega t$ and of $\sin \omega t$

$$R_s = \theta + \eta/\sqrt{\omega} + (g\gamma\lambda M/2\epsilon)(\cos\varphi + \sin\varphi) \quad [70]$$

$$1/C_s = \eta\omega^{\frac{1}{2}} + (g\gamma M/\lambda)(\cos\varphi - \sin\varphi). \quad [71]$$

We shall define an impedance Z^{IV} by means of the two equations

$$R_s^{IV} = (g\gamma\lambda M/2\epsilon)(\cos\varphi + \sin\varphi) \quad [72]$$

$$1/C_s^{IV} = (g\gamma M/\lambda)(\cos\varphi - \sin\varphi). \quad [73]$$

Noting from equation [66] that

$$\sin\varphi = s/(1 + 2s + 2s^2)^{\frac{1}{2}} \quad [74]$$

$$\cos\varphi = (1 + s)/(1 + 2s + 2s^2)^{\frac{1}{2}} \quad [75]$$

it follows that

$$R_s^{IV} = \frac{\gamma g(1 + 2s)}{\sqrt{2\epsilon\omega}(1 + 2s + 2s^2)} \quad [76]$$

$$C_s^{IV} = \frac{\sqrt{2\epsilon}\,(1 + 2s + 2s^2)}{g\gamma\sqrt{\omega}}. \quad [77]$$

The equivalent parallel forms of this impedance are a little simpler. They are

$$R_p^{IV} = \frac{\sqrt{2}\,\gamma g}{\sqrt{\epsilon\omega}\,(1 + 2s)} \quad [78]$$

$$C_p^{IV} = \frac{1}{\gamma g}\sqrt{\frac{\epsilon}{2\omega}}. \quad [79]$$

At all frequencies the variation with frequency of C_p^{IV} is the same as that for a Warburg impedance; at high frequencies (low values of s) the variation of R_p^{IV} is the same as that of the Warburg impedance, and the same is true of C_s^{IV} and R_s^{IV}. At all frequencies

$$R_s^{IV} C_s^{IV}\omega = 1 + 2s \quad [80]$$

which is to be compared with equations [41] and [61].

In acid solutions (or wherever hydronium ions are reduced, rather than water) β will not be negligible and a certain amount of Warburg impedance will be expected to be present, as explained in connection with substances of class III. Therefore the complete equivalent circuit for the case in question is represented as in Fig. 4, where -IV- is a symbol for the impedance Z^{IV} defined by equations [72] and [73]. As before, the Warburg impedance is expected to disappear relative to θ in neutral or alkaline solutions. Also as before,

solution to the differential equation involved. The results will be presented if it should appear that any actual case might correspond to the conditions of the equation.

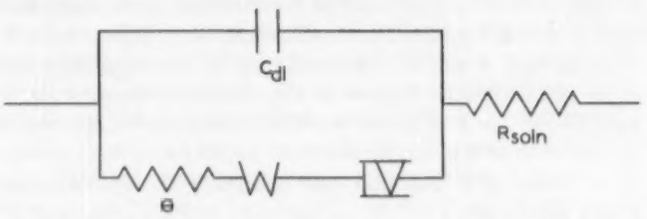

FIG. 4. Equivalent circuit for a system containing substances of class IV.

the series capacity at high frequencies approaches the double layer capacity and the series resistance approaches the solution resistance.

If the substance of class IV under consideration diffuses only into the metallic phase (as is the case with hydrogen atoms) and not into the solution phase, then there is no need to consider a double layer effect analogous to that in equation [45] *et seq.* This follows because the double layer effect there considered affects only substances in the nonmetallic phase. Otherwise it is necessary to restrict the application of the equations for the Z^{IV} impedance to cases where the effect is eliminated by the presence of an excess of an inert electrolyte. It is comparatively easy to derive the appropriate equations for the more general case by the methods already used, but this has not been done since there is little likelihood of their ever being useful.

γ can be evaluated as before through equations [63a] and [63b].

Substances of Class V

In case a substance S in solution is formed only slowly from another substance S_1, also in solution, and supposing S to be directly involved in the electrochemical reaction, (what is commonly called the potential-determining substance) and reversibly reducible, and supposing further that in the absence of any current S and S_1 are in equilibrium, then the substance S may be said to belong to class V. This is the case studied in some detail by Gerischer (8). The impedance Z^V corresponding to the substance S has been derived by him for the case where diffusion coefficients of S and S_1 are the same, and assuming no continuous faradaic current. The expression obtained by Gerischer contains the square root of a complex number. We shall put it into more convenient form by introducing the identity

$$(a + ib)^{\frac{1}{2}} = \left(\frac{\sqrt{a^2 + b^2} + a}{2}\right)^{\frac{1}{2}} + i\left(\frac{\sqrt{a^2 + b^2} - a}{2}\right)^{\frac{1}{2}}.$$

Making this substitution in Gerischer's equation [44], separating real and imaginary parts of the resulting expression, and equating these to the resistive and capacitative parts of the impedance Z^V gives

$$R_s^V = \frac{RT}{n^2\mathbf{F}^2 Q}\,\frac{1}{({}_oc_1 + q_o c)\sqrt{D\omega}} \cdot \left(\frac{q}{\sqrt{2}} + \frac{{}_oc_1}{{}_oc}\,\frac{1}{\sqrt{2(a^2 + 1)(\sqrt{a^2 + 1} - a)}}\right) \quad [81]$$

$$1/C_s^V\omega = \frac{RT}{n^2\mathbf{F}^2 Q}\,\frac{1}{({}_oc_1 + q_o c)\sqrt{D\omega}} \left(\frac{q}{\sqrt{2}} + \frac{{}_oc_1}{{}_oc}\left\{\frac{\sqrt{a^2 + 1} - a}{2(a^2 + 1)}\right\}^{\frac{1}{2}}\right) \quad [82]$$

where $a = k_o/\omega$ and the nomenclature is otherwise that of Gerischer, namely Q = area of the interface; ${}_oc_1$ = concen-

tration of S_1 in the solution at equilibrium; c = concentration of S in the solution at equilibrium; D = diffusion coefficient of both S and S_1 (assumed equal); $q = \nu_1 p_1/\nu p$; ν and ν_1 = stoichiometric factors in the chemical equation $\nu S + \nu_2 S_2 \rightleftharpoons \nu_1 S_1$; p and p_1 = reaction orders in the expression for the rate of the above reaction, namely $v = k_1 c^{p_1} - k c^p$; k_e = value of k (reaction rate constant) at equilibrium in above expression.

These equations define the impedance associated with the substances S and S_1. The equivalent circuit will be like that already shown in Fig. 4 except that we shall have an impedance -V- in place of the impedance -IV-.

The qualitative significance of these results has been discussed by Gerischer and need not be repeated here. Their basic significance is that they give rise to a means of studying the mechanism of electrochemical reactions which are preceded by a rate-determining step in solution. Two applications of the method are given by Vetter (11).

Substances of Class VI

Substances of class VI are those which are present in quantities so small that they do not exhibit the properties of the same substances in bulk. Let Y designate a substance of this class and let y be its concentration at the interface, expressed in units of coulombs per unit area. (This does not imply that Y is a charged substance. It means that the concentration is expressed in equivalents per unit area times Faraday's constant $\mathbf{F}$.) Then $y = \int i dt$, and it proves to be unnecessary to specify the constant of integration. Then since $i = i_e + a \sin \omega t$,

$$y = \int i_e \, dt + a \int \sin \omega t \, dt \qquad [83]$$

$$dy/dt = i_e + a \sin \omega t. \qquad [84]$$

The quantity i_e makes no contribution to the impedance because it has no component of frequency $\omega/2\pi$, and even if i_e varies slowly with time, as it usually will when substances of this class are being formed, the component of frequency $\omega/2\pi$ is negligible, for the same reasons as those mentioned earlier in connection with substances of class II. Thus for the present purposes

$$dy/dt = a \sin \omega t \qquad [85]$$

and combining this result with equation [19] gives for the characteristic impedance associated with the presence of a substance of class VI

$$1/C_e^{\text{VI}} = \partial E/\partial y, \qquad \text{a constant as far as its dependence upon frequency is concerned}$$

$$R_e^{\text{VI}} = 0.$$

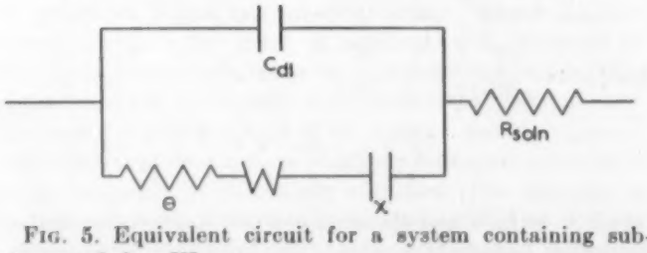

FIG. 5. Equivalent circuit for a system containing substances of class VI.

Then if the other substances present belong to classes I and II, as will be usual, the equivalent circuit will be as shown in Fig. 5. Here we have let $1/\chi = (\partial E/\partial y)_i$, etc., and its value is given approximately by[20]

$$C_e^{\text{VI}} = \chi = \frac{n\mathbf{F}y}{RT} \frac{i_{av}}{\bar{i}}. \qquad [86]$$

The order of magnitude of a lower limit to C_e^{VI} can be found if one considers a monolayer to be composed of about 10^{15} molecules or atoms. Then since $i_{av}/\bar{i}$ cannot be less than α (and will generally be much greater), C_e cannot be less than about 3000 $\mu f/\text{cm}^2$, and will ordinarily be much greater. Except when y is very small (a small fraction of a monolayer), substances of class VI will therefore behave like substances of class I, for which C_e is effectively infinite and R_e is zero.

Discussion

Because of the precision with which impedance measurements can be made in the range of audio frequencies, it is natural to suppose that such measurements can be used to obtain important information about the metal-solution interface. The foregoing analysis may be looked upon as an effort to ascertain what information can be obtained in this way. The conclusion is that under certain carefully chosen conditions such measurements do indeed give quantitatively significant data about electrode processes, but that little or no information is obtained from measurements made upon systems chosen at random. In this respect the situation is very different from that which obtains at the interface between mercury and solutions of inert electrolytes, where almost any choice of electrolyte is permissible and meaningful. The difference arises from the fact that it is not at present possible to obtain truly smooth, homogeneous, and clean surfaces of solid metals, and on this account much care is needed in choosing experimental conditions for which this defect will matter least. In one sense the inhomogeneity and lack of smoothness of a surface are more serious handicaps than the lack of cleanliness, since the equations derived above do not demand a clean surface, but do demand a homogeneous smooth one.

An immediate use which can be made of the equations derived in this paper, apart from their obvious and important use with mercury, is as a test for the smoothness of a solid metallic surface. The theory is sufficiently straightforward to make it possible to state with confidence that smooth surfaces will show no appreciable faradaic admittance at potentials well removed from the half-wave potential. This is evident from Fig. 2, where it is seen that the parameter which controls the faradaic admittance is everywhere large at potentials significantly removed from the half-wave potential. Now all forms of faradaic admittance exhibit the phenomenon of dispersion (variation of apparent capacity and resistance with frequency) when measured with a series bridge or its equivalent, whereas the nonfaradaic admittance does not show this phenomenon when experimental errors are sufficiently well eliminated. Nevertheless some dispersion is al-

[20] This result assumes that $\partial \vec{i}/\partial y = 0$ and $\partial \overleftarrow{i}/\partial y = \overleftarrow{i}/y$. Neither of these can be exactly true, but both must be approximately true. The first is approximately valid because the potential energy of an atom or molecule of Y is not much affected by its neighbors on a homogeneous surface, making its potential energy almost independent of the coverage. The second equation assumes that $\overleftarrow{i}$ is proportional to the coverage. This is probably not true beyond a monolayer, but by that time C_e^{VI} is so large that the corresponding impedance is negligible anyway.

ways observed with solid electrodes even outside the range of potentials for which it might be attributed to the faradaic admittance. This dispersion varies from sample to sample and is noticeably greater on samples which have been subjected to a very slight etching process. All of the results are intelligible if one assumes the dispersion to be primarily a geometric effect attributable to the lack of smoothness on the part of the electrode. With most metals it is found that the dispersion is not markedly a function of the potential, which is just what one would expect from a roughness effect, but not at all what one would expect from the faradaic admittance.

It is generally found that the dispersion is greater on wires and sheets than on spheres of the same metal. This is probably attributable to the fact that wires and sheets of a metal cannot be made smooth so easily as small spheres formed by fusion. In addition, it is more difficult to satisfy the symmetry requirements with wires or sheets than with spheres.

If the object of a given investigation is to measure the capacity of the electrical double layer at the interface between a given solid metal and an electrolyte, it is not altogether necessary to strive for maximum smoothness, because extrapolation to infinite frequency will give the same results whether the surface is smooth or rough. What *is* necessary is to strive for maximum cleanliness of the surface, because the effects of surface films are not diminished by a change of frequency.

It was shown above that as the frequency is increased the series resistance approaches that of the solution. This makes it possible to ascertain that resistance with accuracy for use in such measurements as overvoltage measurements where a correction must be made for the IR drop in the solution. The resistance can be measured with great accuracy for this purpose, especially when the faradaic current is not too large, and since it is also possible to ascertain the current with all desired accuracy, a correction can be made for the IR drop in the solution. This method is believed to be preferable to the measurement of the same quantity by the current-interrupter method.

A brief discussion of the effect of surface films may be helpful. In the presence of substances which are adsorbed as a film on the electrode, the impedance of the system will depend very markedly upon whether the film is an electronic conductor, an ionic conductor, or neither. In the last-named case the capacity of the double layer will be much decreased, R_{soln} will be unaffected, and there will be no faradaic current. (The substance will be a perfect corrosion inhibitor.) If the film is an *ionic* conductor, θ will be much increased, but its significance will remain unchanged and the foregoing analysis likewise. It is especially to be noted that R_{soln} is not thereby altered and neither is the Warburg impedance at equilibrium. This result has been observed experimentally by Randles (6).

If the film is an *electronic* conductor, its resistance is added to that of the solution and all the parameters of the equivalent circuit are altered except Z^V and the Warburg impedance at equilibrium for that component which does not have to diffuse through the film. Except for these two, the parameters of the equivalent circuit depend upon the character of the electronically conducting surface at which the electrochemical reaction takes place.

REFERENCES

1. M. Wien, *Ann. Physik*, **58**, 37 (1896).
2. E. Warburg, *Ann. Physik*, **67**, 493 (1899); **6**, 125 (1901).
3. F. Krüger, *Z. physik. Chem.*, **45**, 1 (1903).
4. T. R. Rosebrugh and W. L. Miller, *J. Phys. Chem.*, **14**, 816 (1910).
5. G. Jones and S. M. Christian, *J. Am. Chem. Soc.*, **57**, 272 (1935).
6. J. E. B. Randles, *Disc. Faraday Soc.*, **1**, 11 (1947).
7. B. Ershler, *Disc. Faraday Soc.*, **1**, 269 (1947); *J. Phys. Chem. U.S.S.R.*, **22**, 683 (1948).
8. H. Gerischer, *Z. physik. Chem.*, **198**, 286 (1951).
9. D. C. Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946).
10. H. Gerischer and K. Vetter, *Z. physik. Chem.*, **197**, 92 (1951) and references there cited.
11. K. Vetter, *Z. physik. Chem.*, **199**, 285, 300 (1952).
12. R. Parsons and J. O'M. Bockris, *Trans. Faraday Soc.*, **47**, 914 (1951).
13. A. Frumkin, *Acta Physicochim.*, **18**, 23 (1943).
14. D. C. Grahame, *Chem. Revs.*, **41**, 441, 496 (1947).
15. A. Frumkin, *Disc. Faraday Soc.*, **1**, 57 (1947); *J. Phys. Chem. U.S.S.R.*, **24**, 244 (1950).
16. D. C. Grahame, Document 2195 of the American Documentation Institute, 1719 N St., N. W., Washington 6, D. C.
17. P. Dolin and B. Ershler, *Acta Physicochim. U.R.S.S.*, **13**, 747 (1940).
18. P. Dolin, B. Ershler, and A. Frumkin, *Acta Physicochim. U.R.S.S.*, **13**, 779 (1940).
19. P. Dolin, A. Frumkin, and B. Ershler, *Acta Physicochim. U.R.S.S.*, **13**, 793 (1940).
20. K. Rosenthal, P. Dolin, and B. Ershler, *Acta Physicochim. U.R.S.S.*, **21**, 213 (1946).
21. D. C. Grahame, *J. Am. Chem. Soc.*, **63**, 1207 (1941).
22. B. Ershler and M. Proskurnin, *Acta Physicochim. U.R.S.S.*, **6**, 195 (1937).

Extra December Issues Available

Additional copies of the December—Theoretical Electrochemistry Issue—of the Journal are available at the office of The Electrochemical Society, Inc., 235 West 102nd Street, New York 25, N. Y.

Price $1.00 per copy to members, $1.25 to non-members. Early placement of orders is recommended.

FUTURE MEETINGS OF
The Electrochemical Society

New York, April 12, 13, 14, 15, and 16, 1953

Sessions on

Electric Insulation, Electronics, Electrothermics,

Theoretical Electrochemistry

Headquarters at the Statler Hotel

* * *

Wrightsville Beach, N. C., September 13, 14, 15, 16, and 17, 1953

Headquarters at the Ocean Terrace Hotel

* * *

Chicago, May 2, 3, 4, 5, and 6, 1954

Headquarters at the La Salle Hotel

Papers are now being accepted for the meeting to be held in New York. Abstracts (not exceeding 75 words in length) are due at the Secretary's Office, 235 West 102nd Street, New York 25, N. Y., *not later than February 1, 1953.* Complete manuscripts should be sent in triplicate to the Editor of the JOURNAL at the same address.

Current Affairs

Local Sections Start Season with Well-Planned Meetings and Large Attendance

Chicago Section

The Chicago Section began its 1952–53 season with a meeting on October 1 at the Chicago Engineers' Club.

The guest speaker, Thomas Comer of Distillation Products Industries, Division of Eastman Kodak Company, Rochester, addressed the group on the subject "High Vacuum Metallizing.

Mr. Comer noted the increasing importance of high vacuum metallizing as a metal finishing process. He then gave a very good exposition of the subject in which he supplemented his description of the theory and practice with examples of the applications and results. The topic was of such interest as to draw guests from as far away as Milwaukee.

New officers of the Chicago Section elected at the final spring meeting, are as follows:

Chairman—Simon P. Gary
Vice-Chairman—Howard T. Francis
Secretary—Robert R. Banks
Treasurer—Werner Jacobson

ROBERT R. BANKS, *Secretary*

Cleveland Section

A joint meeting of the Cleveland Sections of The Electrochemical Society, American Chemical Society, American Institute of Chemists, American Institute of Chemical Engineers, and Alpha Chi Sigma was the occasion of the Cleveland Section's opening meeting of the current season, held on October 16 at the Hotel Hollenden. These five societies, sponsors of the Fourth Annual Dinner of the Chemical Profession in Cleveland, heard Dr. Farrington Daniels, Chairman of the Chemistry Department at the University of Wisconsin, speak on "Our Energy Sources of the Future."

Dr. Daniels, who is president-elect of the American Chemical Society, was Director of the Metallurgical Laboratory, Manhattan District, University of Chicago, in 1945–46. His fields of research include chemical kinetics, photochemistry, photosynthesis, oxides of nitrogen, atomic energy, and solar energy.

Dr. Daniels pointed out that, at present, we are using up the fossil fuels, coal, oil, and gas, at about the rate of 15×10^4 kilogram calories per

DR. FARRINGTON DANIELS

person per day. The rate of use of these stored solar fuels has increased greatly during the last 50 years and is expected to continue to increase. On the basis of our best guesses, he believes these fuels should last another two or three thousand years before complete depletion.

The speaker said that the use of atomic energy is still expensive, cumbersome, and dangerous to personnel for universal use. Some of these difficulties will be overcome but the sources of usable material are still more limited than fossil fuels even though uranium prospecting is the 20th century gold rush and many new deposits are being discovered.

The only source of unending energy, said Dr. Daniels, is the sun. He pointed out that it is universal. In only a few weeks the sun bestows upon the earth as much energy as has been stored up in fossil fuels in all time. At present, solar energy is being used as water power and in food. Supplementing the talk were illustrations of some experimental installations of wind machines, focussing mirrors, and heat storage schemes such as Na_2SO_4 and of pebbles.

The hope for the future, Dr. Daniels says, seems to be in the more efficient use of solar energy, especially for plant growth. At present it is about 0.1 per cent efficient. He believes that it could be raised to 3.0 per cent. Even if it were very much less than this amount it would still be adequate.

JOSEPH M. MARGOLIS, *Secretary*

New York Metropolitan Section

The New York Metropolitan Section opened the new season with an unusually well attended meeting at the Holley Hotel on October 1. The gathering was addressed by Charles W. Eichrodt, Metallurgist, of Phelps Dodge Refining Corporation, Maspeth, N. Y., who spoke on "Electrolytic Copper Refining." He was well qualified to discuss this subject, having served with various mining enterprises in the Southwest and in Chile previous to joining the Phelps Dodge organization.

The audience was augmented by the presence of many members of the local section of the American Institute of Mechanical Engineers who were especially invited because of the nature of the topic under discussion.

Mr. Eichrodt competently covered the subject of electrolytic copper refining from the standpoint of history, world production statistics, tank room practice, effect of impurities in the electrolyte, materials of construction, addition agents, series versus multiple system, anode passivity, and many other factors. He held the attention of his audience so well that although the formal meeting broke up at an unusually late hour, many members remained to offer informal discussion for an even longer period of time.

F. A. LOWENHEIM, *Secretary-Treasurer*

Niagara Falls Section

An informal "mixer" meeting, held on September 9 at the Youngstown Yacht Club, opened the 1952–53 season of the Niagara Falls Section.

Sixty members and guests enjoyed refreshments, a buffet supper, speedboat rides by courtesy of one of the local industries, and an informal talk given by Clarence F. Luck, Supervisor of Public Relations, Western Division, New York Telephone Company, on "Advances in Communications Techniques."

Mr. Luck traced the growth of the telephone system from its beginnings in 1876 to its present total of 46,000,000 telephones in this country and 66,000,000 in the world. Long distance communication has been particularly dependent upon technical advances, he said, such as development of better and smaller loading coils, the application of the De Forest vacuum tube for amplification, use of miniature vacuum tubes of low heat output, and application of the microwave radio relay system. This last, while receiving much publicity in connection with the television network, was primarily developed for telephone communication.

One of the more recent developments Mr. Luck stated, is the transistor, capable of 100,000-fold amplification with small power input, long life, small space requirements, and with little heat output to be dissipated. It is expected that transistors will soon be used in some long lines. Another development is the thermistor, where conductivity depends upon temperature and is applied in long lines to compensate for temperature variations and thus prevent distortion.

Mr. Luck accompanied his talk with demonstrations and a display of the components discussed.

M. JANES, *Secretary-Treasurer*

San Francisco Section

The San Francisco Section met for dinner at the St. Julien Restaurant, San Francisco, on October 8, and later heard an address on "Finishing of Aluminum" by G. H. Kissin, Head of Metal Finishing Department, Division of Metallurgical Research, Kaiser Aluminum & Chemical Corporation, Spokane, Wash.

Dr. Kissin reviewed some of the historical background in the processes of aluminum finishing and followed this with a fairly detailed discussion of the procedures and practices involved in the cleaning and anodizing of aluminum for the purpose of improving the corrosion resistance.

The process of color anodizing was discussed at considerable length and a wide range of samples illustrating the range of colors available were shown. Specimens of various specialized surface treatments were shown by the speaker, and their handling problems were reviewed. These included the Alrok process, the Allodine process, the photoetching, and the buffing and chemical brightening process. All in all, Dr. Kissin gave an excellent review of a portion of the field of aluminum finishing.

H. F. MYERS, *Secretary-Treasurer*

Washington-Baltimore Section

The current season began for the Washington-Baltimore Section with its meeting on October 16, held at the National Bureau of Standards in Washington.

Following a short business session, Dr. Seymour Senderoff of the National Bureau of Standards gave an interesting talk on "Electrolytic Preparation of Molybdenum from Fused Salts." Dr.

DR. SEYMOUR SENDEROFF

Senderoff described his equipment and process, and discussed some of the theoretical aspects of the problem. Of particular interest was the discussion of the effect of the operating variables on the purity and physical structure of the molybdenum deposits.

The process, he said, has been operated only on a laboratory scale to produce molybdenum powders of varying particle size. The deposits have been up to 99.9 per cent molybdenum with as little as 0.02 per cent oxygen.

The animated discussion following the talk indicated the considerable interest in the report.

FIELDING OGBURN, *Secretary-Treasurer*

India Section

The third Technical Meeting of the India Section for 1952 was held on August 4, at the Indian Institute of Science, Bangalore, with Professor M. S. Thacker in the chair. Dr. B. K. Ram Prasad of Electric Grid Office, Government of Bombay, delivered a lecture on "Recent Developments in the Plant and Equipment Used in the Electrochemical-Metallurgical Industries."

The speaker stated that during the next five years power generation in India will increase considerably and the cost of energy will have to be somewhat reduced, thereby making it possible to expand the electro-chemical-metallurgical industries, chiefly alkali-chlorine, aluminum, ferroalloys, etc.

Some of the recent developments in equipment were then outlined: mercury cells for production of high purity caustic, various types of rectifiers, soderberg electrodes, high frequency induction and power frequency furnaces, use of gas turbines direct-coupled to d-c generators for supply of power in aluminum production, and use of subterranean steam in volcanic regions to generate power. Dr. Prasad suggested that a symposium on alkali-chlorine might be arranged by the Section, in view of the fact that the development of the alkali-chlorine industry is expected to be very important in this country in the future. After a lively discussion, the meeting terminated with a vote of thanks to the speaker.

J. BALACHANDRA, *Secretary-Treasurer*

Promat Division Joins Sustaining Members

The Promat Division of Poor and Company, located in Waukegan, Illinois, was recently welcomed by the Society to its list of sustaining members. The parent company is one of the world's largest railroad suppliers.

The Promat Division is engaged in the development, manufacture, and sale of chemical, electrochemical, and ceramic products and processes for the metal finishing industry.

This Division was organized in 1938 and by its extensive research and development program throughout the years has established its products in every country of the free world where metal finishing is practiced.

The Promat laboratories are among the most completely equipped in the chemical, electrochemical, and ceramic

fields and its highly trained technical staff is one of the finest.

A. E. Chester, well known in the chemical industry, is Vice-President and Director of Research, and executive officer of this Division.

The development of high speed zinc addition agents, chromate finishes, vitreous coatings, and chemicals for the preparation of metal surfaces for inorganic and organic coatings are but a few of the products manufactured by this company.

Eastern Plant for Beckman Instruments

Beckman Instruments, Inc., South Pasadena, California, manufacturer of scientific and industrial instruments and precision components, has started construction on a new 20,000 square-foot building, located at Mountainside, New Jersey.

The new plant is to be used as Eastern sales and service offices for the parent company and as a manufacturing facility for the Beckman subsidiary, Helipot Corporation, makers of helical potentiometers.

Monsanto to Build New Hq Office

Immediate start of construction of the new headquarters office building for the Monsanto Chemical Company, in St. Louis County, was authorized recently by the Board of Directors of the company.

The initial building, which is expected to be completed within two years, is part of an over-all plan to accommodate Monsanto's needs for many years. It will be of contemporary design, eight stories high and the initial unit will contain about 350,000 square feet. No manufacturing operations will be conducted at the countysite.

New Atomic Research Lab for Walter Kidde

Walter Kidde Nuclear Laboratories have announced that they are establishing new laboratory facilities on Long Island, near Garden City, to serve as headquarters for the firm's operations.

The research and development laboratory, located at 975 Stewart Avenue, was ready for occupancy about November 1. Research operations were scheduled to start on that date, although the installation of certain specialized equipment will continue for several months.

A minimum staff of 100 will be required when the laboratory is in full operation within six to 12 months.

Among the activities to be undertaken at the laboratory are: corrosion studies in connection with liquid metals and under special conditions encountered in the atomic field; measurement of physical and thermodynamic properties; development of special types of instruments and instrumentation systems; application of liquid metals as heat transfer elements; and measurements with radioactive sources.

News in the Educational Field

Electrochemistry Colloquium at M.I.T.

At an Electrochemistry Colloquium which is being held at Massachusetts Institute of Technology, on Wednesday afternoons from October 8, 1952 to January 14, 1953, a large number of Electrochemical Society members and authors appear on the roster of lecturers. It will be of interest to our readers to note the scope of the program, and the speakers:

CALENDAR

Oct. 8, 1952—"Determination of Isoelectric Point of Silver Iodide in Aqueous Solutions"—Professor Jan T. G. Overbeek, University of Utrecht, Holland.

Oct. 15—"Anodic Polarization of Passive and Non-Passive Chromium-Iron Alloys"—Professor Herbert H. Uhlig, Department of Metallurgy.

Oct. 22—"Coulometric Chemical Analyses"—Professor Lockhart B. Rogers, Department of Chemistry.

Nov. 5—"Electrochemical Investigations on Silver Sulfide"—Professor Carl Wagner, Department of Metallurgy.

Nov. 13—(Professor George Scatchard, Department of Chemistry, will address the Northeast Section of A.C.S. on "Some Electrochemical Properties of Ion Exchange Membranes").

Nov. 19—"Recent Studies on Hydrogen Overvoltage with the Dropping Mercury Electrode"—Professor A. de-Béthune, Department of Chemistry, Boston College.

Dec. 3—"Thermodynamic Properties of the Electrical Double Layer"—Professor David C. Grahame, Department of Chemistry, Amherst College.

Dec. 10—"A Study of Iodide-Iodine Solutions with the EMF Centrifuge"—Dr. D. A. MacInnes, Rockefeller Institute for Medical Research.

Dec. 17—"Some Electrochemical Aspects of Transistor Science"—Dr. Morgan Sparks, Bell Telephone Laboratories.

Jan. 7, 1953—"Thermodynamics of Irreversible Processes Applied to Electrokinetics"—Professor Jan T. G. Overbeek, University of Utrecht, Holland.

Jan. 14—"Streaming Potential Measurements on Quartz"—Douglas Fuerstenau, Department of Metallurgy.

Research Grants by National Research Corp.

The National Research Corporation Scientific Trust has recently made the following grants for the support of research:

Northwestern University, Dr. James N. Pitts, Jr., Assistant Professor, Department of Chemistry, "Photochemical Studies in the Far Ultraviolet and Schumann Regions," $4,000.

Rensselaer Polytechnic Institute, Kent D. Lawson, Instructor, Physics Department, "High Frequency Resonances in Ferrites," $3,480.

Rijks University, Leiden, Holland, Dr. Anton E. van Arkel, Professor, Inorganic Chemistry, "Reactions of Halides or Oxides with Metals," $3,125.

Corrosion Short Course at U. of California

The University of California, at Berkeley, in cooperation with the National Association of Corrosion Engineers, will hold a five-day short course in corrosion February 2–6, 1953. The course is given by the university's extension department and the departments of mechanical engineering, mineral technology, and chemical engineering.

Speakers from industrial and governmental laboratories and academic institutions will discuss subjects covering basic corrosion science theory and application of corrosion mitigation measures.

New Metallurgy Department

The increased demand for industrial scientific research in the field of metallurgy has led to the establishment of a department of metallurgy at Southwest Research Institute, San Antonio, Texas.

Dr. Robert J. Anderson has been appointed to head the department which is undertaking industrial metallurgical research in foundry practice, process metallurgy, and physical metallurgy in addition to studies in metal economics.

DIVISION NEWS

Theoretical Division

The Theoretical Division will elect officers to serve for a two-year term at its business meeting, to be held at the Spring Meeting in New York City. Their term will extend from the end of the Spring Meeting 1953 to the end of the Spring Meeting 1955.

The Nominating Committee, consisting of H. H. Uhlig, Chairman, E. L. Eckfeldt, Arthur Fleischer, and Norman Hackerman, has proposed the following nominations:

Chairman—J. Paul Fugassi, Carnegie Institute of Technology, Pittsburgh, Pa.

Vice-Chairman—André J. deBéthune, Boston College, Boston, Mass.

Secretary-Treasurer—L. B. Rogers, Massachusetts Institute of Technology, Cambridge, Mass.

Additional nominations may be made by ten active members of the Division, in writing to the Secretary-Treasurer or by individual members from the floor at the business meeting. Such nominations should carry the assurance of the nominee's willingness to serve.

WALTER J. HAMER, *Chairman*

PERSONALS

LEONARD WRAY, formerly of Bomac Electrotype Company, Toronto, Canada, has accepted a position as chemist with Atomic Energy of Canada Ltd., Chalk River, Ontario.

JOHN A. RICKETTS has been appointed Assistant Professor of Physical Chemistry in the Chemistry Department of De Pauw University, Greencastle, Ind. Dr. Ricketts had been doing graduate work at Western Reserve University.

MILTON J. ALLEN has joined the staff of CIBA Research Laboratories, Summit, N. J., as head of the Physical Research Department. Dr. Allen had been connected with the National Cancer Institute, Bethesda, Md.

JAMES J. MCINTYRE has been transferred from the position of plant manager of the Memphis, Tenn.. plant of The Electrochemicals Department, E. I. du Pont de Nemours & Co. to assistant director of production at the company's plant in Wilmington, Del.

J. C. WARNER, president of Carnegie Institute of Technology, Pittsburgh, and Electrochemical Society president, has been appointed by President Truman to membership on the General Advisory Committee to the Atomic Energy Commission for a six-year term. Also appointed were Eugene P. Wigner of Princeton University and James B. Fisk of Bell Telephone Laboratories. The new group replaces three scientific experts whose terms have expired.

CHARLES ALLEN THOMAS, president of Monsanto Chemical Company, St. Louis, was presented with the Gold Award in *Financial World's* 1951 competition, at a dinner attended by 1300 persons at the Hotel Statler, New York, on October 28. The award, given for the best annual report of all industry, was made after completion of the 12th annual survey in which 5,000 reports were judged.

WILLIAM N. DUNLAP, formerly with the U. S. Army Chemical Corp., Royal Oak, Mich., is presently employed as supervisor, Plating Laboratory, Chrysler Tank Engine Division, Michoud Ordnance Plant, New Orleans, La.

WILLIAM O. DIPIETRO is now with High Vacuum Equipment Corp., Hingham, Mass. He was formerly with National Research Corp , Cambridge, Mass

MORRIS FEINLEIB of Argonne National Laboratories, Chicago, Ill., has accepted a position with Kaiser Aluminum & Chemical Corp., Process Metallurgy Department, Division of Metallurgical Research, Spokane, Wash.

GEORGE W. HEALY has left Union Carbide & Carbon Company, Research Laboratories, Niagara Falls, N. Y., to join Electro Metallurgical Company, Metallurgical Department, in that city.

JOHN B. PERKINS has accepted a position with the U. S. Rubber Company, as senior engineer in the Chemical Engineering Group of the Technical Department, Kankakee Unit of the Joliet Arsenal, Joliet, Ill.

GEORGE KEELERIC has resigned from United Drill & Tool Corp., Chicago, Ill., to become a consultant, specializing in electrolytic grinding and machining. He is located at 3418 N. Knox Avenue, Chicago.

BRAM C. FELDMAN has been apponted chief engineer at Sundry Electric, Inc., Warren, Pa. Mr. Feldman came from General Electric Company, Syracuse, N. Y.

ROBERT E. MEEKER, winner of the John W. Marden Prize, who is now doing graduate work at Northwestern University, Chicago, Ill., has been awarded an Abbot research assistantship in chemistry.

KENNETH B MEYER of National Lead Company's Research Laboratory, Chappaqua, N. Y., has been transferred to the Fernald Project of National Lead Company in Cincinnati, Ohio.

PHILIP J. CLOUGH of National Research Corporation, Cambridge, Mass., has been promoted from project manager to assistant director of the Metallurgical Department

JUNIOR W. WHITNEY

It was learned only recently that Junior W. Whitney of Fords, New Jersey, passed away on April 28 last.

Mr. Whitney had been employed as development chemist at National Lead Company, Titanium Division, Sayreville, New Jersey. Previously he had served for four years in the U. S. Navy aboard minesweepers, attaining the rank of lieutenant. Mr. Whitney received his B.S. degree in chemistry from Purdue University and the B.S. in chemical engineering from Brooklyn Polytechnic Institute. He joined The Electrochemical Society in 1951.

NEW MEMBERS

In October 1952, the following were elected to membership in The Electrochemical Society:

Active Members

CHARLES H. BROWN, Signal Corps Supply Agency, mailing add: 433 Hansberry St., Philadelphia, Pa. (Battery, Corrosion, Electric Insulation, Electrodeposition, and Electronics)

C. H. CASTLE, Roto Finish Company, mailing add: 1503 Kingston, Kalamazoo, Mich. (Electrodeposition)

HERBERT DAVIS, National Lead Company, mailing add: 20 Waverly Ave., Kenmore, N. Y. (Electrothermic)

SAMUEL B. DEAL, Radio Corporation of America, mailing add: 955 Pleasure Rd., Lancaster, Pa. (Electronics)

HARRY B. GOODWIN, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio (Electrothermic)

RICHARD S. JOHNSON, National Carbon Research Laboratories, P.O. Box 6087, Cleveland, Ohio (Battery and Theoretical Electrochemistry)

NOEL S. KIRBY, Electrolytic Zinc Company of Australia, Ltd., mailing add: Box 634B, G.P.O., Hobart, Tasmania, Australia (Industrial Electrolytic)

ROGER J. METZLER, c/o Handy & Harman, 82 Fulton St New York, N. Y. (Battery)

WILBUR C. MYERS, The Brush Development Company, mailing add: 2401 Malden Rd., Cleveland, Ohio (Corrosion and Electrodeposition)

STEWARD W. O'REAR, Atomic Energy Division, Explosives Dept., E. I. du Pont de Nemours & Co., Wilmington, Del. (Electro-Organic)

HORACIO PEREZ, Instituto Electroquimico, mailing add: Classificador 979, Santiago, Chile (Battery, Electrodeposition, and Industrial Electrolytic)

ALLEN S. RUSSELL, Aluminum Research Laboratories, Freeport Rd., New Kensington, Pa. (Industrial Electrolytic)

ROBERT D. WALKER, JR., University of Florida Libraries, Serials Dept. E-S, Gainesville, Fla. (Battery and Theoretical Electrochemistry)

Associate Member

ALFRED T. KLEINSTEUBER, Carbide and Carbon Chemicals Company, mailing add: 237 S. Purdue, Oak Ridge, Tenn. (Industrial Electrolytic)

Reinstatement

JOSEPH A. ORSINO, National Lead Company Research Laboratories, 105 York St., Brooklyn, N. Y. (Battery)

BOOK REVIEW

PRODUCTION OF ELEMENTAL PHOSPHORUS BY THE ELECTRIC FURNACE METHOD. Chemical Engineering Report #3. Compiled by R. B. Burt and J. C. Barber, 1952. For sale by Treasurer, Tennessee Valley Authority, Knoxville, Tennessee. xii plus 308 pages, $2.00, paper bound.

This is the third report in a series of publications describing the chemical engineering activities of the Tennessee Valley Authority. It is a comprehensive treatment of 308 pages, containing fifty tables and 132 figures or diagrams. It describes preliminary experimental work and large scale development electric phosphorus furnaces and their operation. It discusses utilization of furnace by-products, operation costs, and a general valuation of the electric furnace process for the production of phosphorus. This monograph should be of great interest to those in the electroprocess industries.

R. M. BURNS

EMPLOYMENT SITUATION

Please address replies to box shown, c/o The Electrochemical Society, Inc., 235 W. 102nd St., New York 25, N.Y.

Position Wanted

CHEMICAL ENGINEER, D.Ch.E., P.E., well grounded in chemistry, mathematics, physics. Four years process development in electrochemistry, corrosion, metallurgy, and metal finishing. Three years development in atomic energy and radiology. Desires Research and Development in Greater New York City area. *Reply to Box 351.*

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These secondary standards have been in continuous use for the past *twenty-eight* years by a highly respected clientele. Basic standards of comparison at the Harleco Laboratories have not been permitted to deviate in that entire period of time.

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LITERATURE FROM INDUSTRY

ATKOMATIC ELECTRIC VALVES. Bulletin gives information on industrial applications of Atkomatic Solenoid Valves which are now available for pressures up to 3,000 lb/in.^{2} Special feature is the adjustable timing on the closing stroke which is available to pressures of 300 lb/in.^{2} This eliminates shock on supply lines, particularly on hydraulic operations. The Atkomatic Valve Co. P-81

SPECTROPHOTOMETERS, COLORIMETERS. 20-page booklet lists complete line of Coleman instruments and accessories. Includes automatic titration equipment, *p*H meters, colorimeters, spectrophotometers, nephelometers. Also lists an economical vacuum oven and equipment for mercury purification. Ask for "Waco Catalyst Vol. IX." Wilkens-Anderson Co. P-82

MAGNETIC RECORDING HEADS. The publication "Brush Strokes," for March 1952, describes the development of multichannel magnetic recording heads. General requirements are discussed, then the construction and properties of several such heads are described. "Brush Strokes" for June 1952 outlines "Some Considerations in the Design of Piezolectric Microphones," describing some basic considerations that arise when mechanical elements are joined to acoustical elements. Then follows the detailed working out of the design of a simple Rochelle Salt crystal "Bimorph" microphone and of two simple ceramic "Bimorph" microphones. The Brush Development Co. P-83

PURIFICATION OF METAL SALT SOLUTIONS. Recent bulletin entitled "Purification of Metal Salt Solutions with Hydrogen Peroxide" gives complete directions for isolating metal salts from process solutions used for the following purposes: Electrolytic Nickel Plating; Beryllium Production; Magnesium Production; Phosphatizing; Optical Glass Production containing Lanthanum Salts; and Tin Recovery from Non-Ferrous scrap. BECCO Sales Corp. P 84

VOLTAGE REGULATED POWER SUPPLIES. New condensed bronchure illustrates and describes a range of Kepco Voltage Regulated Power Supplies. Of interest to everyone using electrical and electronic equipment. Kepco Laboratories, Inc. P-85

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X-RAY ANALYSIS. 8-page booklet titled "Facts and Figures on Three Powerful X-Ray Tools for Non-Destructive Analysis" is available gratis. Diagrams show the principles of operation, and data is given on recommended fields of application and results to be obtained. North American Philips Co., Inc P 92

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How to Determine Impurities in Copper Plating Baths

SILVER in copper plating baths may be determined colorimetrically, by using a carbon tetrachloride solution of dithizone to produce the colored solution. The hue measured is that of the mixed color of silver keto dithizonate and cupric keto dithizonate. Small amounts of certain other metals do not interfere, nor is separation of the silver required.

CHLORIDE, also, may be determined colorimetrically. The method depends upon the addition of a known quantity of silver ions and determining the excess of silver ions remaining after silver chloride has been precipitated. The excess is determined by the mixed color of silver and cupric dithizonate.

LEAD traces are determined as follows: Organic material is oxidized with phosphoric acid and the lead is separated from interfering ions by extracting with a carbon tetrachloride solution of dithizone in the presence of potassium cyanide. Transmittance of the solution is measured and the quantity of lead determined from a calibration curve.

CHROMIUM: To determine chromate chromium, nitric acid is added to oxidize any reducing agents, phosphoric acid is added to make a complex with Fe^{+++}, and diphenylcarbazide is added to form a colored complex. Transmittancy of the solution is measured, and the amount of CrO_3 present as chromate is read off the calibration curve.

For total chromium analysis, iron is first removed by precipitation. The chromium is oxidized first by fuming with perchloric acid and then by boiling with ammonium persulfate in the presence of silver ions. The silver is precipitated. The solution is centrifuged, the transmittancy of the clear supernatant solution measured, and the amount of CrO_3 present is determined from the calibration curve.

NICKEL can be accurately determined colorimetrically by forming nickel dimethylglyoxime but copper must first be removed quantitatively.

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